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STRUCTURAL DETERMINATIONS OF SOME TRANSITION METAL HYDRIDO, AND *TRIS*(BENZENE-1,2-DITHIOLATO) COMPLEXES

by

Ⓒ MARTIN COWIE

A THESIS
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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled STRUCTURAL DETERMINATIONS OF SOME TRANSITION METAL HYDRIDO, AND *TRIS*(BENZENE-1,2-DITHIOLATO) COMPLEXES submitted by MARTIN COWIE in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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DATE: Dec 17/73

TO MY PARENTS

ABSTRACT

The crystal and molecular structures of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ have been determined. The central Re_2Si_2 clusters are similar in both molecules and form a rhombus with a Re-Re bond across the shorter diagonal. The Re-Si bond lengths in both compounds are all similar, and are therefore consistent with the hydrogen ligands being terminally bound to the rhenium atoms rather than bridging the rhenium-silicon bonds. The mode of bonding of the hydride ligands is discussed in relation to other similar systems.

The crystal and molecular structures of three *tris* (benzene-1,2-dithiolato) complexes, $(Mo(S_2C_6H_4)_3$, $[As(C_6H_5)_4][Nb(S_2C_6H_4)_3]$ and $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3])$ have been determined in an attempt to explain the stability of the trigonal prism with respect to the octahedron. In the molybdenum and niobium complexes the metals are surrounded by six sulfur atoms in trigonal prismatic coordination. The zirconium complex, however, has a coordination which is best described as a distorted octahedron. The increase in S-C distances, observed through this series, indicates an increasing tendency of the ligands towards the reduced $S_2C_6H_4^{2-}$ formulation. This ten-

dency is discussed in relation to a molecular orbital scheme for trigonal prismatic dithiolenes (by Gray *et. al.*) and is correlated to the destabilization of the prism which is observed progressing through this series.

A disorder in $Re_2(CO)_8[Si(C_6H_5)_2]_2$, involving a small translation of the complete molecule along the crystallographic *b* axis, was investigated in order to ascertain the effect on molecular geometry and thermal parameters.

PREFACE

This thesis presents the results of two independent problems. The first section deals with a structural study of a particular class of transition metal hydrides. The second section is concerned with the structures of transition metal complexes of ligands coordinated through sulfur atoms. The same technique, namely single crystal X-ray diffraction, was used for both problems. The theoretical and experimental details of X-ray diffraction are described in several standard reference texts.[1,2,3,4]

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CHAPTER I: TRANSITION METAL HYDRIDE

INTRODUCTION

The discovery of the first transition metal hydride complexes,[5,6] $FeH_2(CO)_4$ and $CoH(CO)_4$, in the 1930's marked the beginning of approximately twenty years of controversy concerning the structures of hydride complexes and the mode of bonding of the hydrogen atoms in these complexes.

The first electron diffraction study[7] on gaseous $CoH(CO)_4$ and $FeH_2(CO)_4$ led to the conclusion that the metals were surrounded tetrahedrally by the carbonyl groups. The hydrogen atoms were assumed to be bound to the oxygen atoms of the carbonyl groups. Hieber later suggested[8] that the hydrogens were actually bonded to the metals, but were buried in the electron density of the metal and thus had no stereochemical influence.

The infrared spectrum of $CoH(CO)_4$ was initially interpreted[9] as being consistent with the hydrogen atom being primarily bonded to the carbon p_π orbitals at approximately 2.0 Å from the cobalt atom. In this model the hydrogen was believed to be bridging three carbonyl groups. However the findings of Cotton and Wilkinson,[10] based on nuclear magnetic resonance and acid dissociation constants for $CoH(CO)_4$ and $FeH_2(CO)_4$, agreed with Hieber,[8] suggesting that the hydrogens were close to and primarily bonded to the metal atoms. Subsequent L.C.A.O. calculations[11] on $CoH(CO)_4$ yielded the greatest total overlap integral of Co-H and C-H for a Co-H distance of 1.2 Å. This distance was again consistent with the hydrogen being buried in the Co orbitals, since a covalent distance of 1.593 Å had been obtained[12] in CoH.

Since $HMn(CO)_5$ had physical properties[13] similar to $Fe(CO)_5$, its infrared spectrum was interpreted assuming it, like $Fe(CO)_5$, had trigonal bipyramidal coordination,[14,15] with the hydrogen buried in the manganese orbitals and exerting no stereochemical influence. In addition the identification[16] of the Co-H stretching frequency at 1934 cm^{-1} added further proof that the hydrogen was bound to the metal. The large shifts to high field of the proton resonance that were observed in transition metal hydrides were also initially interpreted as evidence for "buried" hydrogens. However subsequent studies[17,18] showed that these shifts were due to more subtle electronic effects and could be explained assuming normal metal-hydrogen covalent distances.

In addition it was shown[19] that the neglect of quadrupole effects which resulted[20,21] in short M-H distances, was not justified.

Thus until 1959 the experimental evidence was interpreted as indicating that the hydrogen atom exerted no stereochemical influence and was buried in the transition metal orbitals.

Discovery of the true coordination in the metal hydride complexes had to await the availability of good quality X-ray and neutron diffraction data and also the discovery of stable crystals of these hydrides [$CoH(CO)_4$ and $FeH_2(CO)_4$ were unstable gases]. In X-ray diffraction studies, since the X-rays are scattered by electrons, hydrogen atoms contribute little to the total scattering. Therefore location of the hydrogen atom requires extremely high quality data, and the difficulty of direct observation of hydrogen atoms increases with increasing atomic number of the atoms present. However, even when the hydrogen atom is not located, its approximate position can be deduced from the coordination of the other ligands. In neutron diffraction the scattering of thermal neutrons is by the nucleus and varies[22] approximately as $A^{1/3}$ (where A is the atomic mass number). Thus the scattering amplitudes of all atoms are of the same order of magnitude, allowing the hydrogen atoms to be located with a precision comparable to that of heavier atoms.

The X-ray structural determinations[23,24] of $PtHBr[P(C_2H_5)_3]_2$ and $OsHBr(CO)[P(C_6H_5)_3]_3$ and later[25] of α-$HMn(CO)_5$ failed to locate the hydrogen atoms but showed the empty coordination sites where the hydrogens were probably located. In the X-ray crystallographic study[26] of $RhH(CO)[P(C_6H_5)_3]_3$, however, the hydrogen atom *was* located, at 1.72(15) Å from the rhodium atom, a distance consistent with the sum of the rhodium and hydrogen covalent radii.[27] (The reliability of this hydrogen identification has recently been challenged.[28] However the original paper[26] clearly outlined the conditions that would favour the direct observation of hydrogen atoms in heavy atom structures and provided the impetus for crystallographers to attempt hydrogen atom location.)

Neutron diffraction experiments[29,30] on K_2ReH_9 and also β-$HMn(CO)_5$ proved unequivocally that the hydrogens acted as typical ligands and were not buried in the metal orbitals. The Re-H distances average 1.68(1) Å and the Mn-H distance is 1.601(16) Å in these compounds.

It was a fortunate sequence of events that the molecular structure[31] of $RhH[P(C_6H_5)_3]_4$ was not determined prior to those mentioned above. Otherwise the hypothesis that the hydrogen was buried in the metal orbitals might have had a longer lifetime. In this compound the phosphorus atoms form, within experimental error, a regular tetrahedron about the Rh atom. Although it seems that the hydrogen is exerting no stereochemical influence, its influence is just minimized by the bulky $P(C_6H_5)_3$ groups. Comparing for example the volume[32,33,34] of a $P(C_6H_5)_3$ group at - 370 $Å^3$ to that of CO (- 45 $Å^3$)[35] and H (- 7 $Å^3$)[36] it becomes obvious that this distortion is reasonable.

Of the many subsequent transition metal hydride complexes to be studied[35,37,38] some of the most interesting involved bridging hydrogens, where the hydrogen ligands were simultaneously bonded to two atoms. Two main categories of bridging hydrogens exist, the most common being between two transition metals, and the second involving bridging between a transition metal and a non-transition metal. In the former category two types have been observed, involving either a bent or a linear M-H-M bond.

A linear M-H-M bond[39,40] was deduced in the structure of $Cr_2H(CO)_{10}^-$. Although the hydrogen atom position was not located, stereochemical and bonding arguments suggest that it is collinear with the two chromium atoms and equidistant from each. [It is to be noted, however, that the X-ray data cannot differentiate between two possibilities: either the hydrogen is bonded symmetrically to both chromium atoms (single-minimum potential well), or it is preferentially bonded to one chromium atom (double-minimum potential well) and is "tunnelling" between the two sites.] The observed Cr···Cr distance of 3.41(1) Å is considerably longer than the Cr-Cr bond length[39] of 2.97(1) Å in $Cr_2(CO)_{10}^{2-}$ and yields a Cr-H distance of 1.70 Å which is in good agreement with the other known metal-hydrogen distances. The hydrogen ligand then occupies the sixth coordination site of each $Cr(CO)_5$ fragment giving the anion D_{4h} symmetry. The insertion of the hydrogen ligand causing the two $Cr(CO)_5$ moieties to be further apart also results in the carbonyl groups being eclipsed, compared with the staggered carbonyls in $Cr_2(CO)_{10}^{2-}$. More recently a linear Re-H-Cr bond has also been inferred[41] in $(OC)_5ReHCr(CO)_5$. Although the hydrogen was not located it was considered to be collinear with the Re and Cr atoms, since again the two metalpentacarbonyl groups are eclipsed and since the least squares planes containing the equatorial CO groups are within 2.5° of being parallel. The Re-Cr distance is 3.435(1) Å, which is again consistent with hydrogen insertion between the two metals.

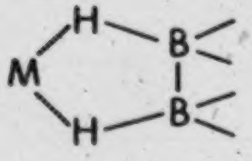
Bent M-H-M bonds have been deduced in several complexes. In $Re_3H(CO)_{12}^{2-}$ and $Re_3H_2(CO)_{12}^{-}$ the triangular species[42,43] contain an isosceles triangle of rhenium atoms with Re-Re distances of ~ 3.04 Å and 3.17 Å, with the longer distances presumably being bridged by the hydrogen ligands. These bent hydrogen bridges were confirmed recently[44] in the analogous $H_3Mn_3(CO)_{12}$ complex, in which the hydrogen atoms were located. The manganese atoms form an equilateral triangle with the hydrogen ligands symmetrically bridging the triangle edges. The average Mn-Mn distance is 3.111 Å compared with 2.923 Å in $Mn_2(CO)_{10}$[45] and thus again shows the lengthening of the bridged metal-metal bond, a feature which has been used as evidence for hydrogen bridging in the rhenium clusters.[42,43] The average Mn-H distance is 1.72 Å.

In $Re_2MnH(CO)_{14}$[46,47] and $Re_3H(CO)_{14}$[48] the hydrogen ligands are located between the rhenium atoms in a position which is almost collinear with these atoms. However the estimated Re-H-Re angles, calculated assuming octahedral coordinations, are 164° in $Re_2MnH(CO)_{14}$ and 159° in $Re_3H(CO)_{14}$.

The structure[49] of $Mo_2H(CO)_4(\pi\text{-}C_5H_5)_2[P(CH_3)_2]$ consists of two $(\pi\text{-}C_5H_5)Mo(CO)_2$ fragments joined at the Mo atoms by a symmetrically bridged $P(CH_3)_2$ group and presumably by a hydrogen atom. The structure[50] of $Mn_2H(CO)_8[P(C_6H_5)_2]$ closely resembles that of $Mo_2H(CO)_4(\pi\text{-}C_5H_5)_2[P(CH_3)_2]$ with two carbonyl groups on each metal replacing a $(\pi\text{-}C_5H_5)$ group. However, in the manganese compound the hydrogen atom *was* located, in the position equivalent to that postulated in the molybdenum complex, with a Mn-H distance of 1.86(6) Å and a Mn-H-Mn angle of 104(5)°.

Hydrogen bridging three metal atoms has been postulated in $Ru_6H_2(CO)_{18}$[51] and $Rh_3H(\pi\text{-}C_5H_5)_4$.[52,53] The ruthenium structure consists of an octahedron of Ru atoms each bound to three terminal carbonyl groups. The hydrogen ligands appear to occupy two opposite faces of the octahedron. In $Rh_3H(\pi\text{-}C_5H_5)_4$ the equilateral triangle of Rh atoms has one cyclopentadienyl ring bonded to each Rh with the fourth ring parallel to the rhodium triangle. The hydrogen ligand is then postulated as being equidistant from each Rh on the opposite side of the triangle from the fourth C_5H_5 group.

Hydrogen bridging between a transition metal and a non-transition metal has been observed in boron complexes with the hydrogen bridging the boron and the transition metal. Three basic types exist:



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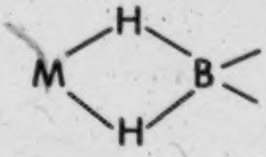

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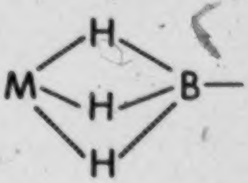


III

Structures of type I were observed in $Mn_3H(BH_3)_2(CO)_{10}$,[54] $Cu(B_3H_8)[P(C_6H_5)_3]_2$[55] and $Cr(B_3H_8)(CO)_4^-$.[56,57,58] In the manganese compound all hydrogen atoms of the BH_3 group are coordinated to a Mn atom and in addition a bent Mn-H-Mn bond exists between the two $Mn(CO)_3$ moeities. In $Cu(B_3H_8)[P(C_6H_5)_3]_2$ the coordination of the copper atom is a distorted tetrahedron with two of the coordination sites occupied by bridging hydrogens. The P-Cu-P and H-Cu-H angles of 120° and 103° respectively, reflect this distortion. $Cr(B_3H_8)(CO)_4^-$ has an octahedrally hybridized chromium atom with two sites again being occupied by bridging hydrogens.

Coordination of type II is exhibited[59,60] by $Cu(BH_4)[P(C_6H_5)_3]_2$. The copper geometry again is distorted tetrahedral with two hydrogen atoms of the borohydride group bridging the copper and boron atoms. The short Cu-B distance of 2.184(9) Å and long Cu-H distance of 2.02(5) Å suggests delocalized bonding between the copper atom and the borohydride group in which direct Cu-B overlap might be significant.

In $Zr(BH_4)_4$[61] the molecule is crystallographically required to possess T_d symmetry. The zirconium atom is tetrahedrally surrounded by the four boron atoms, and one terminal hydrogen atom is located on each C_3 axis. So it appears that M-H-B bonding of type III is present with the Zr atom surrounded by twelve H atoms.

The reactions of disubstituted silanes with dirhenium decacarbonyl and with both tungsten and molybdenum hexacarbonyls produced an interesting series of silicon-bridged, metal-metal bonded species which were also postulated as containing hydrogen-bridged metal-silicon bonds.[62,63] Since this was only the second class of compounds in which hydrogen was postulated as bridging a transition metal-non-transition metal bond, a systematic study of the representative molecules from this series was therefore undertaken to elucidate the major structural characteristics of the systems.

Viewing only the central cluster and ignoring the carbonyl groups, the molecules fall into five major classes:

I. no hydrogen ligands,[64] e.g. $Re_2(CO)_8[Si(C_6H_5)_2]_2$,

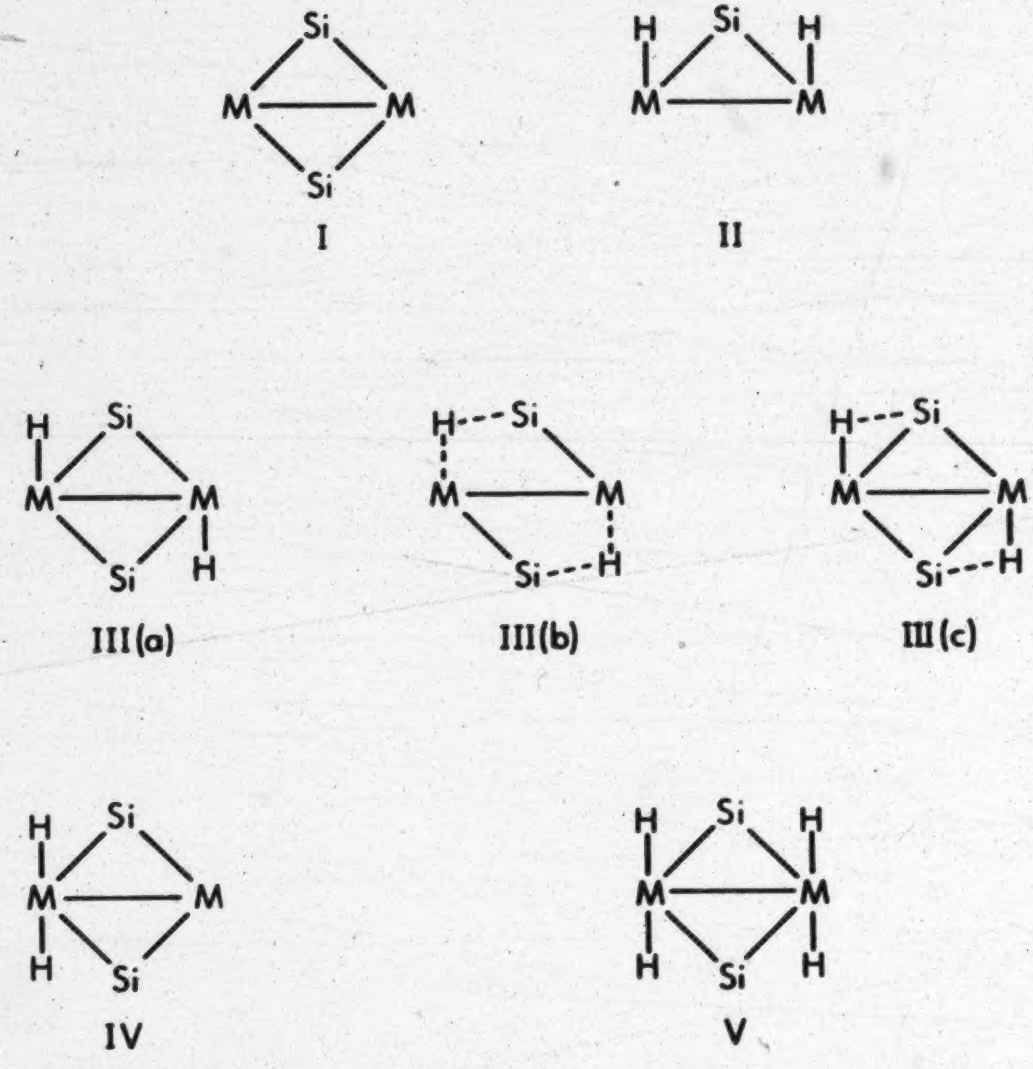
II. two hydrogens, each on different transition metals but adjacent to the same silicon atom[62,65] e.g. $Re_2(CO)_8H_2Si(C_6H_5)_2$,

III. two hydrogens, each on different transition metals and adjacent to two different silicon atoms,[66] e.g. $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$,

IV. two hydrogens, both on the same transition metal but adjacent to different silicons, e.g. $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, and

V. four hydrogens, two attached to each transition metal, each silicon having two adjacent hydrogens, e.g. $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

The structural fragments are shown in Fig. 1 using valence bond description and normal terminal transition metal hydride formulation, with the exceptions of III(b) where bridging hydrogens are indicated and III(c) where the terminal hydrogens interact weakly with the silicon atoms. The main interest in this series centred around the central cluster of transition



I

II

III(a)

III(b)

III(c)

IV

V

Fig. 1: CENTRAL FRAMEWORKS OF THE SILICON-BRIDGED TRANSITION METAL SERIES.

metal and silicon atoms, especially when hydrogen ligands were present, to obtain information concerning the nature of the bonding of the hydrogen ligands.

It had been suggested on the basis of spectroscopic evidence that in these compounds the hydrogen ligands bridged the metal-silicon bonds rather than being bonded terminally to the metals.[62,63] The basis of this argument was the spectroscopic studies by Kaesz and coworkers[67,68] on the trimeric rhenium hydride $[HRe(CO)_4]_3$ and its deuteride $[DRe(CO)_4]_3$, in which the absence of a distinct metal-hydrogen stretching frequency in the infrared was interpreted as evidence that the hydrogens were bridging. Since the terminal metal-hydrogen stretch should be visible in the infrared, its silence was postulated as a characteristic feature of M-H-M bridges. This was extended to the series of transition metal silicon hydrides where the metal-hydrogen stretch was again absent in the infrared,[63] and consequently a Si-H-M bridge was postulated. In addition, in $Re_2(CO)_8H_2Si(CH_3)_2$, the methyl resonance appeared as a 1:2:1 triplet at $\tau = 8.87$ with a coupling constant $J = 1.5$ Hz.[63] The magnitude of this coupling constant also suggested that the high field protons, which are splitting the methyl resonance, were close to the dimethylsilicon moiety since $J(CH_3\text{-}Si\text{-}H) = 4.2$ Hz for dimethylsilane alone.

The first member of this series to have its molecular structure solved by X-ray techniques was $Re_2(CO)_8H_2Si(C_6H_5)_2$.[62,65] Unfortunately, due to the dominance of the rhenium scattering, location of the hydrogen ligands was not possible. However, the coordination sites adjacent to the metal-silicon bonds were conspicuously vacant so the approximate locations of the hydrogens were apparent. Elder postulated[65] that the hydrogens were located in the Re_2Si plane such that the Re-Re-H angle was 90°. Thus for a rhenium-hydrogen bond length[29] of 1.68 Å, a silicon-hydrogen bond length of 1.59 Å would result. This position he said would give the proper orientation for a three centre Si-H-Re bond.

However, the subsequent structure determination of the non-hydridic species $Re_2(CO)_8[Si(C_6H_5)_2]_2$[64] showed a remarkable similarity in Re-Si bond lengths [2.542(3) Å] with $Re_2(CO)_8H_2Si(C_6H_5)_2$, [2.544(9) Å], which was not expected if a three centre two electron Si-H-Re bond is involved in the latter. An unambiguous comparison of the two structures was hindered, however, by the realization that a disorder problem was present in $Re_2(CO)_8[Si(C_6H_5)_2]_2$ (see Appendix 1). Although it was not believed that this would affect the bond lengths in the central Re_2Si_2 cluster, it did cast some doubt on accurate comparisons of the two compounds.

Further evidence favouring the three centre Si-H-M bond arose from the structural determination of $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$,[66] [type III(b) in Fig. 1] in which two differing tungsten-silicon bonds were found [2.586(5) Å and 2.703(4) Å]. This was interpreted as being due to hydrogen insertion in the tungsten-silicon bond, thus forming a three centre W-H-Si bond. Therefore the crystal and molecular structure determinations of members IV and V ($Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$) were undertaken to obtain further information concerning the bonding of the hydrogen ligand in this series. These structure determinations are described in Chapters II and III.

CHAPTER II: THE CRYSTAL AND MOLECULAR STRUCTURE OF DIHYDRIDO TRICARBONYL RHENIUM *BIS* (μ-DIETHYLSILICON) DIHYDRIDO TRICARBONYL RHENIUM, $[Re_2(CO)_6H_4(Si(C_2H_5)_2)_2]$.

EXPERIMENTAL

The sample of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ which was kindly supplied by Dr. Graham and Mr. Hoyano[63] was recrystallized from normal hexane, yielding colourless crystals with the shape of a general parallelepiped. Preliminary photography indicated only Laué symmetry $\bar{1}$ indicative of a triclinic space group. The systematic absences for the working cell, as determined by Weissenberg (0kℓ, 1kℓ, 2kℓ: CuK$_{\bar{\alpha}}$ X-radiation), and Precession methods (h0ℓ, h1ℓ, h2ℓ, hk0, hk1, hk2: MoK$_{\bar{\alpha}}$ X-radiation), are hkℓ: $h + k = 2n + 1$, $h + \ell = 2n + 1$, $k + \ell = 2n + 1$, and are consistent with the non-standard space groups F1 and F$\bar{1}$. The non-standard cell was retained as the working cell for its convenience with respect to the crystal morphology and unit cell angles. Precise lattice parameters were obtained at 23°C from an analysis of the setting angles for 18 reflections which had been carefully centred on a Picker manual four circle diffractometer using CuK$_{\alpha_1}$ radiation of wavelength 1.54051 Å.

A Delaunay reduction was performed[69] and failed to show the presence of higher symmetry. The F centred cell parameters are : a = 8.357(3) Å, b = 16.228(6) Å, c = 18.184(6) Å, α = 118.98(2)°, β = 92.62(3)° and γ = 95.44(3)°, and the reduced primitive cell parameters are: a = 8.357(3) Å, b = 8.767(3) Å, c = 8.776(3) Å, α = 109.07(3)°, β = 97.76(3)°, and γ = 112.88(3)°. The reduced primitive cell is related to the F centred cell by: $\underline{a}_P = -\underline{a}_F$, $\underline{b}_P = 1/2(\underline{b}_F + \underline{a}_F)$, $\underline{c}_P = -1/2(\underline{b}_F + \underline{c}_F)$. The observed density [2.23(2) g cm^{-3}] obtained by floatation in aqueous Clerici's solution (Thallous formate-malonate, ρ_{max} = 4.3 g ml^{-1}), is in satisfactory agreement with that calculated on the basis of four molecules in the F centred cell (2.25 g cm^{-3}). For space group F$\bar{1}$ the imposed symmetry on the molecule is $\bar{1}$, while no restrictions are possible for space group F 1. Since $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ can have $\bar{1}$ symmetry, F$\bar{1}$ was chosen and was later verified by successful refinement of the model. The General Equivalent Positions for the space group F$\bar{1}$ are : ±(x, y, z; 1/2 + x, 1/2 + y, z; 1/2 + x, y, 1/2 + z; x, 1/2 + y, 1/2 + z).

Intensity data were collected on the Picker manual diffractometer using CuK$_\alpha$ radiation monochromated by the (002) reflecting plane of an oriented graphite crystal using a take-off angle of 2°. Two crystals were used during data collection and in each case they were aligned with their a* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: crystal 1 - $\{1,0,0\}$, 0.095 mm; $\{0,1,0\}$, 0.065 mm; $\{0,\bar{1},1\}$, 0.084 mm; and crystal 2 - $\{1,0,0\}$, 0.077 mm; $\{0,0,1\}$, 0.065 mm; and $\{0,\bar{1},1\}$, 0.036 mm. Data were collected for reflections with 2θ values between 0° and 125° using the coupled $\omega/2\theta$ scanning technique with a 2θ scan speed of 2°/min and scan width of three degrees (to allow for increase in mosaic spread as crystal decomposition occurred). Stationary background counts were measured at the limits of each scan for 20 seconds. Assuming approximate linearity of background, the intensity of the peak (I) is given by:

$$I = P - t(B_1 + B_2) \tag{1}$$

where P = peak count, $t = t_P/t_B$ or the ratio of peak scan time to the sum of the background times, and B_1 and B_2 are the background counts. Standard deviations of the intensities were computed from the relationship:

$$\sigma(I) = (P + t^2B + p^2I^2)^{1/2} \tag{2}$$

where $B = B_1 + B_2$. An ignorance factor (p) of 0.03 was used to account for machine errors and to prevent unreasonably high weighting being applied to reflections of high intensity.[70] The detector was a scintillation counter and was used in conjunction with a pulse height analyzer which was tuned to accept 95% of the CuK_α peak.

Eight well distributed standard reflections were monitored at approximately 10 hour intervals to investigate possible decomposition. The decomposition was found to be approximately linear with time and was essentially free of $\sin\theta/\lambda$ dependence. The total decomposition for the data collection was about 10%. The 1690 unique reflections collected were reduced to 1510 using the criterion that a peak is significantly above background when $I/\sigma(I) \geq 3.0$. The significant data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. Standard deviations in the structure factors, $\sigma(F)$, were obtained from the expression:[71]

$$\sigma(F) = \frac{1}{2}\sqrt{\frac{D}{ALp'}} \cdot \frac{\sigma(I)}{I^{1/2}} \qquad (3)$$

where D, A, L, and p′ are the decomposition, absorption,[72] Lorentz, and polarization correction factors respectively. The high linear absorption coefficient[86] for $Re_2(CO)_6H_6[Si(C_2H_5)_2]_2$ using $CuK_{\bar{\alpha}}$ X-radiation ($226.07\ cm^{-1}$) gave rise to a wide range of transmission factors (0.138 to 0.382) which made an absorption correction imperative. The absorption correction was verified by observation of the variation in I_{h00} ($\chi = 90°$) as ϕ was varied. The final corrected intensities of this ϕ scan data showed variation from the mean of less than 10% and thus were judged to be internally consistent.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson map[73,74] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, and $0 \leq w \leq 0.5$. The Re-Re, Re-Si, and Si-Si vectors are derived for space group $P\bar{1}$ in Table 1. The vectors for space group $F\bar{1}$ are generated by adding (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) to those derived for $P\bar{1}$. In addition all vector multiplicities increase by a factor of 4. The origin peak is due to the sum of the vectors between every atom and itself, thus the magnitude of the origin vector is roughly given by: $(2 \times 75^2 + 2 \times 14^2 + 6 \times 8^2 + 14 \times 6^2 + 24 \times 1^2) = 12554$. In the Fourier program used to calculate the vector map, however, the origin peak is normalized to 1000. Therefore taking account of the largest negative peak (~ -40), and assuming the temperature factors are comparable, one expects the Re-Re vectors to have approximate magnitude 466, the Re-Si vectors ~ 174 and the Si-Si vectors ~ 17 above background. Viewing the Patterson map (summarized in Table 2) it is obvious that the first two vectors correspond to Re-Re vectors. On inspection of the map the first vector is identified as associated with the 0, 1/2, 1/2 origin therefore is attributed as $(2x_R, 1/2 + 2y_R, 1/2 + 2z_R)$. The coordinates of the rhenium atom are then calculated as (0.120, -0.010, -0.061). The second peak then corresponds to the edge of the vector $(1/2, 1/2, 0) - (2x_R, 2y_R, 2z_R)$.

The next most intense peak, having a magnitude approximately comparable to that expected for a Re-Si vector, was situated at approximately 2.44 Å from the origin (a distance which is similar to the Re-Si distance in $Re_2(CO)_8H_2Si(C_6H_5)_2$[62,65]). For this reason it was chosen as the $(x_R - x_S, y_R - y_S, z_R - z_S)$ vector and from this the silicon coordinates were calculated as (-0.08, -0.13, -0.61). The next two vectors were then identified as $(1/2, 1/2, 0) - (x_R - x_S,$

TABLE 1: DERIVATION OF Re-Re, Re-Si, AND Si-Si VECTORS FOR SPACE GROUP $P\bar{1}$

	x_R, y_R, z_R [a]	$-x_R, -y_R, -z_R$	x_S, y_S, z_S	$-x_S, -y_S, -z_S$
x_R, y_R, z_R	0, 0, 0	$-2x_R, -2y_R, -2z_R$	$-(x_R - x_S)$, $-(y_R - y_S)$, $-(z_R - z_S)$	$-(x_R + x_S)$, $-(y_R + y_S)$, $-(z_R + z_S)$
$-x_R, -y_R, -z_R$	$2x_R, 2y_R, 2z_R$	0, 0, 0	$x_R + x_S$, $y_R + y_S$, $z_R + z_S$	$x_R - x_S$, $y_R - y_S$, $z_R - z_S$
x_S, y_S, z_S	$x_R - x_S$, $y_R - y_S$, $z_R - z_S$	$-(x_R + x_S)$, $-(y_R + y_S)$, $-(z_R + z_S)$	0, 0, 0	$-2x_S, -2y_S, -2z_S$
$-x_S, -y_S, -z_S$	$x_R + x_S$, $y_R + y_S$, $z_R + z_S$	$-(x_R - x_S)$, $-(y_R - y_S)$, $-(z_R - z_S)$	$2x_S, 2y_S, 2z_S$	0, 0, 0

[a] (x_R, y_R, z_R) and (x_S, y_S, z_S) are the coordinates for the rhenium and silicon atoms respectively.

TABLE 2: ASSIGNMENT OF MOST INTENSE PATTERSON VECTORS

u	v	w	RELATIVE PEAK HEIGHT	ASSIGNMENT
0.240	0.480	0.378	487	$(0,1/2,1/2) + (2x_R,2y_R,2z_R)$
0.240	-0.500	0.126	370	$(1/2,1/2,0) - (2x_R,2y_R,2z_R)$[b]
0.200	0.120	0.0	131	$(x_R-x_S,\ y_R-y_S,\ z_R-z_S)$
0.280	0.380	0.0	123	$(1/2,1/2,0) - (x_R-x_S,\ y_R-y_S,\ z_R-z_S)$
0.040	0.360	0.360	119	$(0,1/2,1/2) + (x_R+x_S,\ y_R+y_S,\ z_R+z_S)$
0.240	0.040	0.396	98	Re-C and Re-O vector build-up.
0.480	0.460	0.234	91	
0.0	0.140	0.126	90	$-(x_R+x_S,\ y_R+y_S,\ z_R+z_S)$[b]

[b] shoulder of the peak.

$y_R - y_S$, $z_R - z_S$) and (0,1/2,1/2) + ($x_R + x_S$, $y_R + y_S$, $z_R + z_S$). Image seeking around the Re-Re vectors then identified three of the next four vectors as being due to build-ups of Re-C and Re-O vectors from the molecules at (1/2,1/2,0) and (0,1/2,1/2). The peak observed at -(0.00, 0.140, 0.126) was identified as the edge of the vector - ($x_R + x_S$, $y_R + y_S$, $z_R + z_S$).

At this point it was obvious that the Re_2Si_2 core had an inversion centre or at least was very close to having one, otherwise a more complex vector pattern would have been expected corresponding to independent Re(1), Re(2), Si(1), and Si(2) positions.

A least squares refinement phased on the rhenium and silicon positions converged in two cycles yielding a discrepancy index, $R_1 = 0.132$, and a weighted residual, $R_2 = 0.186$. These "R factors" as calculated in the least squares program are defined as:

$$R_1 = \sum \Big| |F_o| - |F_c| \Big| / \sum |F_o| \qquad (4)$$

$$R_2 = \left\{ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 \right\}^{1/2} \qquad (5)$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively, and w the weighting factor is defined by $w = 1/\sigma^2(F)$.

Structure factors were calculated using the atomic scattering factors [75] for rhenium and silicon atoms to which the anomalous dispersion corrections,[76] both real and imaginary were applied [77] ($\Delta f'_{Re} = -5.58$, $\Delta f''_{Re} = 5.37$, $\Delta f'_{Si} = 0.23$, $\Delta f''_{Si} = 0.36$). The function which was minimized during the least squares refinement was $\Sigma w(|F_o| - |F_c|)^2$.

An electron density difference map, phased on the rhenium and silicon atom positions, yielded the location of all other non-hydrogen atoms. A least squares calculation performed on all non-hydrogen atoms converged in two cycles to $R_1 = 0.061$ and $R_2 = 0.074$. Decomposition and absorption corrections were applied to the data and one further cycle of refinement gave $R_1 = 0.055$ and $R_2 = 0.073$. Comparison of $|F_o|$ and $|F_c|$ showed no indication of extinction problems so no correction was applied. This was reasonable considering the width of the peaks (~ 2°) indicating high mosaicy of the crystals.

Refinement of the model with rhenium and silicon atoms having anisotropic temperature factors gave $R_1 = 0.039$ and $R_2 = 0.053$ after two cycles. An electron density difference map phased on this model showed features in the regions of the other atoms which suggested that they too be given anisotropic temperature factors. This gave $R_1 = 0.034$ and $R_2 = 0.045$ after a further two cycles of refinement. The form of the temperature factors used was:

$$\exp\,[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)].$$

The validity of the anisotropic refinement was verified by a Hamilton's R test[79] at the 0.005 significance level.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map (1.75 - 1.14 e $\mathrm{\AA}^{-3}$) were located in the space between the rhenium and silicon atoms in the approximate position expected for a hydrogen bound to rhenium. For this reason the method of La Placa and Ibers[33] was used in an attempt to discern whether these peaks were hydrogen atoms or just artifacts arising from the improper treatment of the rhenium scattering or vibrations. Ibers reasoned that if the peak is not due to hydrogen scattering, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height would be expected to vary in accordance with the equation

$$\rho_H = \frac{1}{2\pi^2} \int_0^{s_o} (1 + a^2s^2/4)^{-2} \exp(-Bs^2/16\pi^2)s^2 ds \quad (6)$$

where ρ_H is the electron density of the hydrogen atom, a is the Bohr radius = 0.5292 Å, $s = 4\pi\lambda^{-1}\sin\theta$, and B is the hydrogen temperature factor. Using a temperature factor of 3.6, electron density difference maps were calculated for sin θ/λ cut-offs of 0.2, 0.25, 0.3, 0.35, 0.4, 0.58 (Complete Data). The results are summarized in Table 3.

TABLE 3: OBSERVED AND CALCULATED ELECTRON DENSITIES FOR VARYING SIN θ/λ CUT-OFFS

SIN θ/λ LIMIT	NUMBER OF TERMS	$\rho_{CAL.}$ (eÅ^{-3})	$\rho_{OBS.}$ (eÅ^{-3})
0.20	74	0.16	0.49 - 0.42
0.25	143	0.25	0.78 - 0.69
0.30	243	0.33	1.07 - 0.87
0.35	371	0.41	1.25 - 0.97
0.40	556	0.47	1.44 - 1.02
0.58 (Complete Data)	1509	0.63	1.75 - 1.14

The electron density observed is in all cases much greater than that calculated by Ibers' formula. A representation of the electron density difference factors. This gave $R_1 = 0.034$ and $R_2 = 0.045$ after a further two cycles of refinement. The form of the temperature factors used was:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)].$$

The validity of the anisotropic refinement was verified by a Hamilton's R test[79] at the 0.005 significance level.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map (1.75 - 1.14 e Å^{-3}) were located in the space between the rhenium and silicon atoms in the approximate position expected for a hydrogen bound to rhenium. For this reason the method of La Placa and Ibers[33] was used in an attempt to discern whether these peaks were hydrogen atoms or just artifacts arising from the improper treatment of the rhenium scattering or vibrations. Ibers reasoned that if the peak is not due to hydrogen scattering, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height would be expected to vary in accordance with the equation

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0.58 (Complete Data)	1509	0.63	1.75 - 1.14

The electron density observed is in all cases much greater than that calculated by Ibers' formula. A representation of the electron density difference

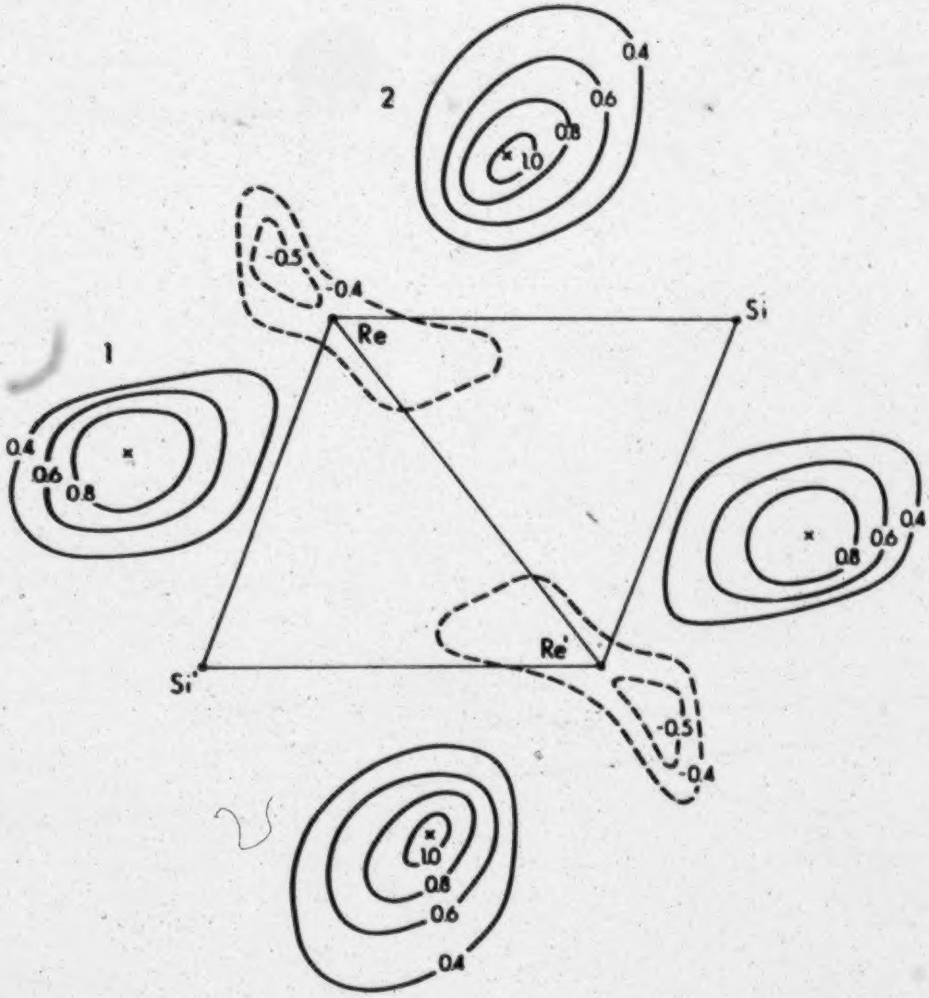
2
0.4
0.6
0.8
1.0
-0.5
-0.4
Re
Si
1
0.4
0.6
0.8
0.4
0.6
0.8
Re'
Si'
-0.5
-0.4
1.0
0.8
0.6
0.4

Fig. 2: ELECTRON DENSITY DIFFERENCE MAP THROUGH THE Re_2Si_2 PLANE [$(\sin\theta/\lambda)_{MAX}$ = 0.35].

map calculated through the plane of the rhenium and silicon atoms for a sin θ/λ limit of 0.35 is shown in Figure 2. The hydrogen, which could be situated anywhere within the 0.4e $\mathring{A}^{-3}$ contour on this diagram, therefore cannot be located with certainty. This implied that the peak height, although being contributed to by the hydrogen, could be receiving a strong contribution due to the inadequacy in description of the rhenium scattering. For this reason several least squares refinements and corresponding electron density difference maps were calculated making changes of ± 0.5 e to each of the real and imaginary parts of the anomalous dispersion corrections in turn. This produced no changes in the refinements or in the difference maps. It was therefore concluded that the peaks, although possibly containing contributions due to the hydrogen atoms, are due mainly to inadequacies of the model or systematic errors in the data. Among these are inadequate description of the scattering due to the rhenium atoms and residual absorption effects. In addition, doubt concerning the degree of contribution of the hydrogen ligands to these peaks existed because of the failure to locate the methylene hydrogen atoms of the ethyl groups.

The computer programmes used in solution and refinement of structure and presentation of Data are listed and briefly described in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 4. The final fractional coordinates of all atoms except hydrogens are shown in Table 5, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic U's[80] and the equivalent isotropic B's[81] of all atoms are shown in Table 6. Relevant bond lengths and bond angles are shown in Table 7. The bond lengths and angles along with their standard deviations were obtained from ORFFE. A packing diagram for the face centred cell, viewed onto the $0k\ell$ plane is shown in Figure 4. The open bonds indicate molecules in the $0k\ell$ plane whereas solid bonds indicate molecules in the $1/2\ k\ell$ plane.

TABLE 4: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 4 (continued)

H	L	FOBS	FCAL
K = 2**			
2	12	1817	1843
2	14	727	756
2	16	360	370
4	-18	1270	1249
4	-16	1000	1050
4	-12	3348	3206
4	-10	1916	1815
4	-8	367	275
4	-6	3781	3909
4	-4	6094	6304
4	-2	2325	2633
4	0	1190	1158
4	2	3488	3611
4	4	3472	3500
4	6	927	929
4	8	1383	1362
4	10	2212	2229
4	12	1633	1650
4	14	296	312
6	-20	1484	1533
6	-18	872	871
6	-16	651	672
6	-14	2216	2080
6	-12	3141	3163
6	-10	1377	1430
6	-8	1610	1625
6	-6	3701	3682
6	-4	3485	3854
6	-2	1115	1202
6	0	1736	1692
6	2	3404	3386
6	4	2067	2026
6	6	1305	1278
6	10	1622	1611
6	12	891	926
8	-20	1205	1238
8	-18	670	670
8	-16	644	682
8	-14	1982	2050
8	-12	2404	2400
8	-10	443	508
8	-8	1299	1301
8	-6	2669	2678
8	-4	3230	2296
8	-2	954	907
8	0	1762	1777
8	2	2904	2840
8	6	1261	1235
8	8	888	871
8	10	1049	1100
10	-20	1026	1112
10	-18	639	668
10	-16	672	658
10	-14	1659	1663
10	-12	1863	1881
10	-10	834	915
10	-8	766	694
10	-6	2081	2076
10	-4	1926	1916
10	-2	623	662
10	0	1222	1207
10	2	2100	2069
10	4	1290	1270
10	6	672	663
12	-18	607	502
12	-16	737	730
12	-14	1978	1967
12	-12	2209	2164
12	-10	473	523
12	-8	1711	1646
12	-6	2366	2297
12	-4	1630	1560
12	0	1590	1607
12	2	2049	2102
12	4	845	878
14	-16	1007	1063
14	-14	1820	1765
14	-12	1069	1058
14	-8	1684	1611
14	-6	1636	1600
14	-4	754	766
14	-2	507	450
14	0	1201	1323
14	2	1065	1107
16	-16	829	826
16	-14	1170	1173
16	-12	696	705
16	-10	311	265
16	-8	1099	1036
16	-6	988	961
16	-4	615	376
K = 3**			
-17	3	308	303
-17	7	696	678
-17	9	827	765
-17	11	368	287
-17	13	377	424
-15	-1	763	822
-15	1	1215	1158
-15	3	795	763
-15	5	391	342
-15	7	1409	1301
-15	9	1257	1216
-15	11	864	905
-15	13	823	897
-15	15	1251	1307
-15	17	1002	1070
-13	-5	677	520
-13	-3	600	517
-13	-1	1478	1502
-13	1	1526	1555
-13	3	593	556
-13	5	1057	1017
-13	7	2299	2160
-13	9	1580	1526
-13	13	1111	1136
-13	15	1663	1662
-13	17	968	990
-11	-7	939	902
-11	-5	316	301
-11	-3	994	982
-11	-1	2133	2161
-11	1	1667	1610
-11	5	1644	1670
-11	7	2582	2603
-11	9	1372	1617
-11	11	323	326
-11	13	1273	1260
-11	15	1580	1575
-11	17	776	797
-11	19	255	321
-9	-9	1109	1097
-9	-7	996	1065
-9	-3	1311	1322
-9	-1	1980	1942
-9	1	1238	1275
-9	5	1757	1730
-9	7	2910	2997
-9	9	1173	1190
-9	11	395	416
-9	13	944	902
-9	15	1378	1364
-9	17	761	782
-9	19	384	347
-7	-11	707	606
-7	-9	1805	1622
-7	-7	1519	1679
-7	-5	516	504
-7	-3	1137	1161
-7	-1	3225	3396
-7	1	2336	2531
-7	5	1937	1956
-7	7	3509	3453
-7	9	2187	2216
-7	13	1592	1560
-7	15	1766	1726
-7	17	854	809
-7	19	373	388
-5	-11	1246	1257
-5	-9	2607	2677
-5	-7	1978	1917
-5	-5	410	421
-5	-3	2589	2770
-5	-1	3776	4085
-5	1	1966	2113
-5	3	593	626
-5	5	3684	3512
-5	7	4630	4263
-5	9	1107	1094
-5	11	1532	1557
-5	13	2049	2030
-5	15	1591	1560
-5	17	420	447
-3	-15	704	738
-3	-11	1834	1746
-3	-9	3120	2996
-3	-7	1572	1612
-3	-5	1071	1117
-3	-3	2893	2993
-3	-1	3366	3508
-3	1	1295	1342
-3	3	1596	1562
-3	5	3788	3543
-3	7	2636	2695
-3	9	401	319
-3	11	1426	1439
-3	13	1959	1923
-3	15	1137	1127
-1	-17	1008	1069
-1	-15	607	698
-1	-13	623	665
-1	-11	1994	1916
-1	-9	3040	3015
-1	-7	1063	1193
-1	-5	1317	1265
-1	-3	2559	2566
-1	-1	2739	2726
-1	1	1083	828
-1	3	1701	1705
-1	5	3082	3230
-1	7	2196	2260
-1	9	638	618
-1	11	1356	1327
-1	13	1702	1757
-1	15	933	939
1	-17	1340	1308
1	-15	837	838
1	-11	1920	1874
1	-9	3451	3282
1	-7	2127	2022
1	-5	1034	1050
1	-3	3406	3290
1	-1	2578	2597
1	1	1303	1458
1	3	1133	1226
1	5	3871	3916
1	7	2598	2593
1	9	267	318
1	11	1275	1268
1	13	1749	1771
1	15	1075	1098
3	-19	1237	1286
3	-17	1778	1785
3	-15	753	731
3	-13	975	963
3	-11	2688	2800
3	-9	3613	3431
3	-7	1282	1182
3	-5	3080	2965
3	-3	4963	5057
3	-1	2310	2756
3	1	252	213
3	3	2755	2848
3	5	3971	4053
3	7	1799	1817
3	9	611	338
3	11	1722	1697
3	13	1723	1761
5	-19	1627	1680
5	-17	1295	1292
5	-13	1262	1213
5	-11	2820	2782
5	-9	2075	2076
5	-7	717	570
5	-5	3095	3206
5	-3	3677	3740
5	-1	1693	1682
5	1	423	397
5	3	2286	2360
5	5	2636	2587
5	7	732	730
5	9	676	657
5	11	1207	1240
7	-19	1280	1307
7	-17	1215	1199
7	-13	1405	1417
7	-11	2052	2035
7	-9	1232	1279
7	-5	2589	2607
7	-3	3454	3601
7	-1	1130	1231
7	3	1502	1465
7	5	1872	1846
7	7	785	776
7	9	372	370
7	11	893	911
9	-19	1284	1305
9	-17	1059	1019
9	-13	1126	1044
9	-11	2328	2335
9	-9	1643	1650
9	-7	372	379
9	-5	2244	2255
9	-3	2677	2668
9	-1	1497	1541
9	1	267	181
9	3	1737	1708
9	5	1702	1659
9	7	559	508
11	-19	1480	1541
11	-17	1063	1087
11	-13	1800	1837
11	-11	2476	2408
11	-9	1185	1156
11	-7	628	605
11	-5	2383	2369
11	-3	2615	2597
11	-1	876	882
11	1	975	965
11	3	1626	1629
11	5	1136	1108
13	-17	452	460
13	-15	660	657
13	-13	1627	1591
13	-11	1513	1531
13	-9	400	348
13	-7	1016	996
13	-5	1732	1716
13	-3	1164	1190
13	1	828	825
13	3	991	1086
15	-15	612	686
15	-13	1057	1069
15	-11	1121	1117
15	-7	613	577
15	-5	964	966
15	-3	769	828
17	-11	990	943
17	-9	301	250
K = 4**			
-16	2	935	982
-16	4	922	892
-16	6	833	711
-16	10	1300	1261
-16	12	830	881
-14	0	1123	1139
-14	2	1545	1561
-14	4	863	775
-14	6	352	328
-14	8	1256	1178
-14	10	1644	1548
-14	12	655	676
-14	14	607	667
-14	16	1046	1100
-12	-6	975	1035
-12	-4	649	662
-12	-2	537	619
-12	0	1327	1316
-12	2	1646	1621
-12	4	796	836
-12	6	577	600
-12	8	1427	1426
-12	10	1162	1219
-12	12	373	330
-12	14	645	603
-12	16	1126	1127
-12	18	757	788
-10	-8	676	678
-10	-6	1140	1156
-10	-4	767	765
-10	-2	666	653
-10	0	1695	1537
-10	2	1822	1844
-10	4	828	853
-10	6	640	639
-10	8	1491	1502
-10	10	1354	1365
-10	12	527	491
-10	14	705	798
-10	16	1377	1365
-10	18	857	867
-8	-8	986	1011
-8	-6	1737	1673
-8	-4	1257	1273
-8	-2	505	469
-8	0	2212	2320
-8	2	2463	2557
-8	4	1125	1165
-8	6	959	930
-8	8	2533	2522
-8	10	1994	1953
-8	12	424	409
-8	14	1047	1030
-8	16	1692	1658
-8	18	1060	1075
-6	-12	538	576
-6	-10	622	591
-6	-8	1920	1871
-6	-6	2324	2310
-6	-4	606	615
-6	-2	1829	1916
-6	0	3170	3295
-6	2	2393	2527
-6	4	648	640
-6	6	2567	2560
-6	8	3660	3594
-6	10	1520	1476
-6	12	357	305
-6	14	1383	1373
-6	16	1760	1762
-6	18	761	761
-4	-14	1044	1153
-4	-12	348	292
-4	-10	1081	1051
-4	-8	2010	1997
-4	-6	1522	1575
-4	-2	1932	2006
-4	0	3439	3556
-4	2	1598	1613
-4	4	582	576
-4	6	2191	2111
-4	8	2091	2021
-4	10	1225	1215
-4	12	392	403
-4	14	1163	1169
-4	16	1296	1137
-2	-16	929	985
-2	-14	1120	1131
-2	-12	366	366
-2	-10	1138	1116
-2	-8	2051	2027
-2	-6	1609	1603
-2	-2	2048	2016
-2	0	3569	3605
-2	2	2191	2082
-2	4	278	229
-2	6	2128	2177
-2	8	3116	3125
-2	10	1169	1186
-2	12	287	279
-2	14	889	903
-2	16	1161	1168
0	-16	1351	1352
0	-14	1330	1318
0	-10	1302	1287
0	-8	3160	3067
0	-6	2497	2416
0	-4	322	223
0	-2	2906	2718
0	0	3966	4226
0	2	2154	2166
0	6	2461	2466
0	8	2974	3018
0	10	1172	1155
0	12	595	563
0	14	1271	1282
2	-18	896	918
2	-16	1652	1692
2	-14	1262	1285
2	-10	2732	2656
2	-8	4643	[illegible]
2	-6	1742	1721
2	-4	1093	1090
2	-2	2986	3106
2	0	3853	4116
2	2	1557	1659
2	4	1359	1369
2	6	2968	2991
2	8	2355	2338
2	10	375	391
2	12	1005	995
2	14	1208	1250
4	-18	1049	1070
4	-16	1629	1591
4	-14	580	600
4	-12	896	894
4	-10	2536	2462
4	-8	3111	3080
4	-6	1061	1100
4	-4	1228	1225
4	-2	2653	2836
4	0	2160	2167
4	2	261	194
4	4	1191	1175
4	6	2077	2010
4	8	1395	1404
4	12	732	798
6	-18	1056	1058
6	-16	1099	1078
6	-14	549	605
6	-12	464	367
6	-10	1884	1908
6	-8	2999	3082
6	-6	1272	1233
6	-4	1053	1051
6	-2	1956	2008
6	0	1802	1830
6	2	881	922
6	4	840	843
6	6	1857	1879
6	8	1236	1267
8	-18	1126	1208
8	-16	1567	1557
8	-14	781	830
8	-12	473	498
8	-10	2320	2372
8	-8	2670	2625
8	-6	811	852
8	-4	1176	1230
8	-2	2395	2457
8	0	1936	1940
8	2	492	369
8	4	1224	1222
8	6	1679	1700
8	8	966	1005
10	-18	1463	1504
10	-16	1575	1607
10	-12	1103	1076
10	-10	2211	2176
10	-8	2065	2029
10	-4	1909	1967
10	-2	2320	2372
10	0	1052	1053
10	4	1178	1165
10	6	1324	1356
12	-18	1194	1263
12	-16	846	877
12	-12	1116	1060
12	-10	1643	1618
12	-8	997	948
12	-6	463	478
12	-4	1639	1671
12	-2	1329	1267
12	0	615	577
12	2	291	278

Table 4 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 5: ATOMIC POSITIONAL PARAMETERS[a]

ATOM	x	y	z
Re	0.11870(5)	-0.01029(3)	-0.06551(2)
Si	-0.0875(3)	-0.1386(2)	-0.0709(2)
C1	0.271(1)	-0.0259(7)	-0.1477(7)
C2	-0.041(1)	0.0202(7)	-0.1282(7)
C3	0.278(1)	-0.0428(8)	-0.0045(7)
C4	-0.409(2)	-0.240(1)	-0.1392(8)
C5	-0.261(1)	-0.1901(8)	-0.1570(6)
C6	-0.006(1)	-0.2389(8)	-0.0638(6)
C7	0.075(2)	-0.3048(9)	-0.1401(8)
O1	0.364(1)	-0.0351(7)	-0.1945(6)
O2	-0.129(1)	0.0377(7)	-0.1691(6)
O3	0.377(1)	-0.0623(8)	0.0298(6)

[a] Standard deviations in parentheses refer to last digit quoted.

TABLE 6: THERMAL PARAMETERS ($\mathring{A}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B^a (\mathring{A}^2)$
Re	0.0380(3)	0.0406(3)	0.0331(3)	0.0010(2)	0.0037(2)	0.0175(2)	2.98
Si	0.0471(14)	0.0394(13)	0.0379(13)	-0.0013(10)	0.0018(10)	0.0176(11)	3.37
C1	0.062(7)	0.048(6)	0.048(6)	-0.006(5)	-0.001(5)	0.021(5)	4.36
C2	0.064(7)	0.043(6)	0.054(6)	0.000(5)	0.013(5)	0.020(5)	4.39
C3	0.052(6)	0.058(6)	0.054(6)	0.004(5)	0.016(5)	0.026(5)	4.35
C4	0.060(8)	0.098(11)	0.068(8)	-0.028(7)	-0.004(6)	0.037(7)	6.38
C5	0.055(6)	0.060(6)	0.045(6)	-0.008(5)	-0.005(5)	0.020(5)	4.53
C6	0.076(8)	0.052(6)	0.046(6)	0.008(5)	0.013(5)	0.027(5)	4.49
C7	0.116(11)	0.068(8)	0.068(8)	0.043(8)	0.028(7)	0.030(7)	6.50
O1	0.086(7)	0.103(8)	0.076(6)	0.004(5)	0.034(5)	0.036(6)	7.19
O2	0.082(6)	0.097(7)	0.063(5)	0.026(5)	-0.003(4)	0.049(5)	5.99
O3	0.054(5)	0.129(8)	0.095(7)	0.024(5)	0.006(4)	0.076(6)	6.53

[a] Equivalent isotopic thermal parameter.

TABLE 7: INTRAMOLECULAR DISTANCES AND ANGLES

INTRAMOLECULAR DISTANCES[a] (Å)

Re-Re'[b]	3.084(1)	Si-C6	1.88(1)
Re-Si	2.533(2)	C1-O1	1.14(2)
Re-Si'	2.535(3)	C2-O2	1.17(1)
Re-C1	1.94(1)	C3-O3	1.17(1)
Re-C2	1.96(1)	C4-C5	1.54(1)
Re-C3	1.97(1)	C6-C7	1.52(2)
Si-C4	1.885(8)		

INTRAMOLECULAR ANGLES[a] (DEGREES)

Re-Re'-C1[b]	178.5(3)	C3-Re-C2	179.1(5)
Re-Re'-C2	91.0(3)	C4-Si-C6	108.5(5)
Re-Re'-C3	89.3(3)	Re-Si-Re'	74.9(1)
Re-Re'-Si	52.6(1)	Re-C1-O1	178.0(9)
Re-Re'-Si'	52.5(1)	Re-C2-O2	175.7(9)
C1-Re-C3	89.4(4)	Re-C3-O3	177.5(9)
C1-Re-C2	90.3(4)	Si-C4-C5	114.5(8)
C1-Re-Si	126.6(3)	Si-C6-C7	115.0(10)
C1-Re-Si'	128.3(3)		

[a] Standard deviations in parentheses refer to last digit quoted.

[b] Primed atoms related by an inversion centre.

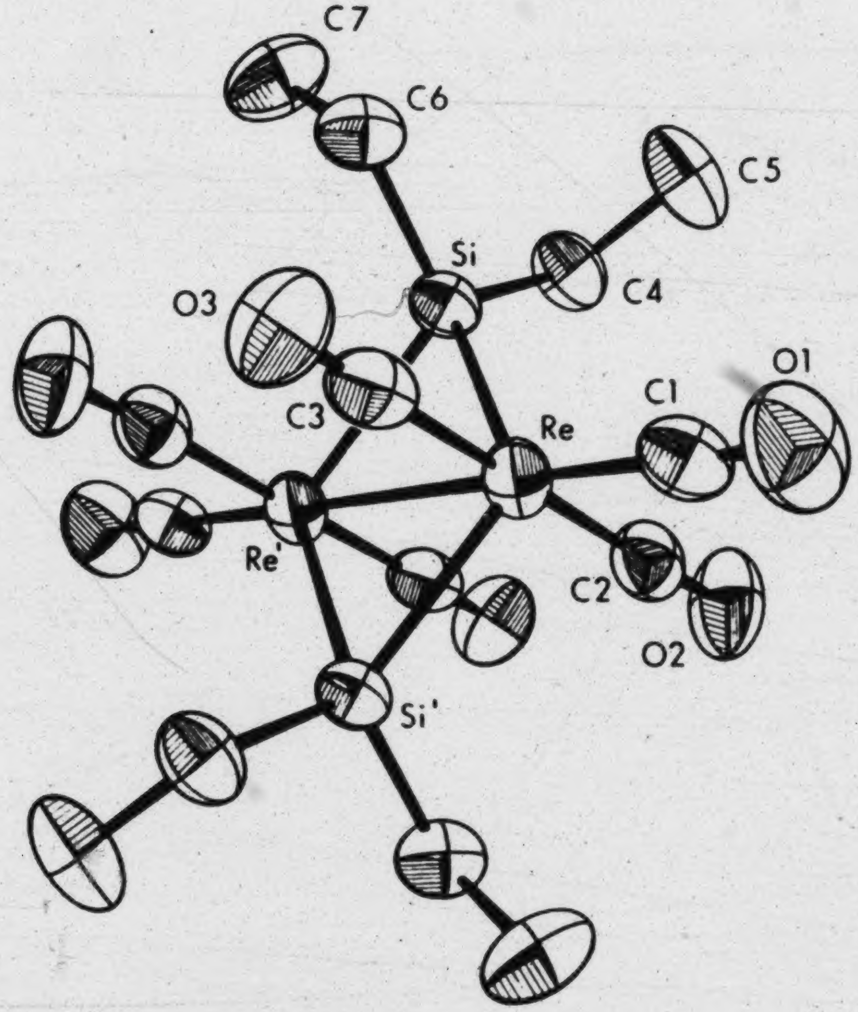
C7
C6
C5
Si
C4
O3
O1
C1
C3
Re
Re'
C2
O2
Si'

Fig. 3: A PERSPECTIVE VIEW OF $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

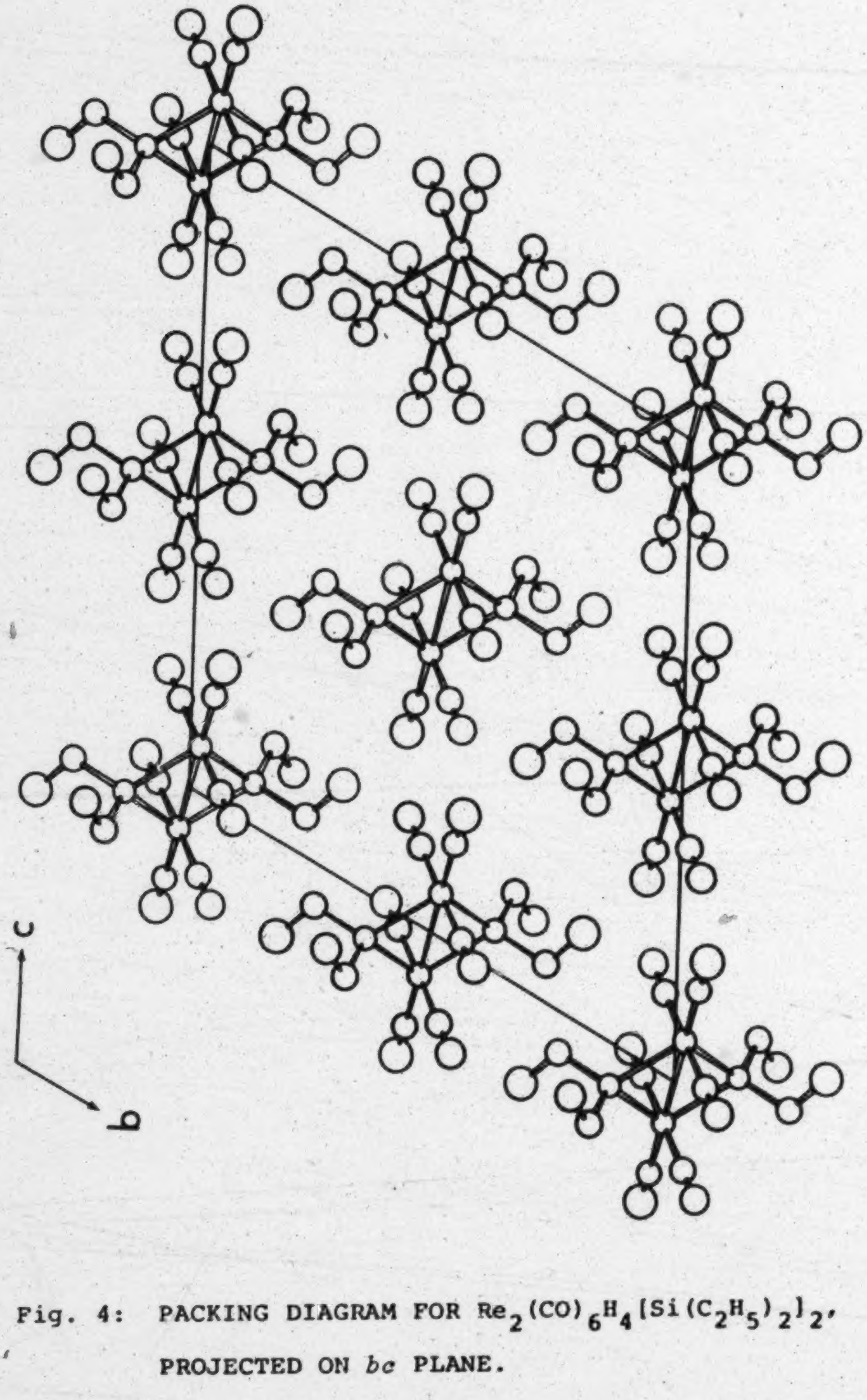

Fig. 4: PACKING DIAGRAM FOR $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$, PROJECTED ON *bc* PLANE.

DESCRIPTION OF STRUCTURE

$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ has approximate C_{2h} molecular symmetry. Its molecular structure is shown in Figure 3. The molecule is composed of a central cluster of two rhenium and two silicon atoms in the shape of a rhombus, with like atoms at opposing corners, and a bond joining the two rheniums across the shorter diagonal. One carbonyl group on each rhenium lies approximately along the Re-Re axis, while the other four lie above and below the plane of the rhombus, two on each rhenium. The ethyl groups are bonded two to each silicon, one above and one below the rhombus plane, giving the silicon atoms a distorted tetrahedral environment.

The Re-Re distance is 3.084(1) Å, compared with 3.121(2) Å in $Re_2(CO)_8H_2Si(C_6H_5)_2$,[62,65] 3.001(1) Å in $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] and 3.02 Å in $Re_2(CO)_{10}$,[45,82,83] and thus is again consistent with a Re-Re single bond. This is further substantiated by the acute Re-Si-Re angle [74.9(1)°]. The average Re-C (carbonyl) distance is 1.96 Å and the average C-O distance is 1.16 Å. These agree well with the carbonyl distances in other rhenium carbonyl derivatives.[62,64,65] The Re-C and C-O bonds along the Re-Re bond are not significantly different from the two *trans* carbonyl groups perpendicular to the Re_2Si_2 plane. In addition the average Si-C (ethyl) distance (1.88 Å) and C-C distance (1.53 Å) both agree with the sums of the Si-C (sp^3) and C(sp^3)-C(sp^3) covalent radii[27,84] (1.91 Å and 1.54 Å respectively).

The Re-Si bond lengths (2.534 Å) are in close agreement with those found in $Re_2(CO)_8H_2Si(C_6H_5)_2$[62,65] and $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] (2.544 Å and 2.542 Å respectively). This was not expected if bridging hydrogens were present in the two hydrides. Rather a difference in bridged and unbridged Re-Si bonds, analogous to that observed in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$[66] was expected. A complete discussion of this phenomenon follows in Chapter IV, with emphasis on the existence of bridging hydrogens and their relation to the transition metal-silicon bonds.

CHAPTER III: THE CRYSTAL AND MOLECULAR STRUCTURE OF DIHYDRIDO TRICARBONYL RHENIUM *BIS* (μ-DIETHYLSILICON) TETRACARBONYL RHENIUM, $[Re_2(CO)_7H_2(Si(C_2H_5)_2)_2]$.

EXPERIMENTAL

The sample of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, supplied by Dr. Graham and Mr. Hoyano,[63] was sublimed in a sealed tube to give crystals that were suitable for a single crystal diffraction study. The crystals produced were clear colourless plates. Preliminary photographs showed $\bar{1}$ Laué symmetry and no systematic absences, consistent with the triclinic space groups $P1$ and $P\bar{1}$. Precise lattice parameters were obtained at 22°C from the 2θ angles of 17 reflections centred on a Picker manual four circle diffractometer using CuK_{α_1} X-radiation (λ = 1.54051 Å). The parameters are: a = 8.664(1) Å, b = 14.066(2) Å, c = 9.343(1) Å, α = 96.57(2)°, β = 93.86(1)°, γ = 91.63(1)°. A Delaunay reduction[69] showed no higher symmetry. The experimental density [2.21(2) g cm^{-3}] determined by floatation in aqueous Clerici's solution, is in acceptable agreement with that calculated (2.23 g cm^{-3}) assuming two molecules of molecular weight 742.9

a.m.u. in a unit cell of volume 1107 $\mathring{A}^3$.

Intensity data were collected on the Picker manual diffractometer using CuK$_{\bar{\alpha}}$ X-radiation monochromated using the (002) reflecting plane of an oriented graphite crystal and using a 2° take-off angle. The crystal was aligned with its a^* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form measured as: {1,0,0}, 7.7×10^{-2} mm; {0,1,0}, 5.3×10^{-2} mm; {0,0,1}, 1.9×10^{-2} mm. A coupled $\omega/2\theta$ scan technique was used with a 2θ scan speed of 2°/min to collect all reflections with $2\theta \leq 125°$. Initially a peak scan of 90 secs. (3 deg.) and a stationary background count of 20 secs. at the limits of the scan were used, however as the crystal decomposed and the mosaic spread increased this was changed to 99 sec. peak scans and 19 sec. backgrounds.[85] A scintillation counter in conjunction with a pulse height analyser, tuned to accept 95% of the CuK$_\alpha$ peak, was used to detect the scattered X-rays. Nine well distributed standard reflections were monitored at approximately 10 hr. intervals to assess decomposition effects. The 2836 unique reflections collected were reduced to

2020 significant observations using the criterion that a peak was significantly above background for $I/\sigma(I) \geq 3.0$, where $\sigma(I)$ was computed as described in Chapter II. The data were then reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. The decomposition was approximately linear with time and no significant sin θ/λ dependence was observed. Total decomposition for the data collection was about 13%. Standard deviations, $\sigma(F)$, in the structure factors were computed as described in the previous chapter using a "p factor" of 0.03.

The high linear absorption coefficient[86] of 216.78 cm^{-1} for $CuK_{\bar{\alpha}}$ X-radiation, and the platey habit of the crystals gave rise to a considerable range of transmission factors (0.14 - 0.47). The absorption correction was verified experimentally by investigation of the behavior of I_{h00} as a function of ϕ. The internal consistency of the corrected intensities showed maximum deviations of less than 10% from the mean and was considered acceptable.

TABLE 8: PATTERSON VECTORS[a] FOR $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$

u	v	w	Multiplicity	Relative Peak Height[c]	Assignment[b]
0.167	0.200	0.080	2	523	$(x_1-x_2),(y_1-y_2),(z_1-z_2)$
0.210	0.500	0.500	2	520	$(x_2+x_1),(y_2+y_1),(z_2+z_1)$
-0.384	0.300	0.403	1	288	$2x_1,\ 2y_1,\ 2z_1$
0.036	0.325	0.414	1	231	$2x_2,\ 2y_2,\ 2z_2$
0.090	-0.150	0.070	2	184	$-(x_1-x_4),-(y_1-y_4),-(z_1-z_4)$
0.254	0.050	0.145	2	169	$(x_1-x_3),(y_1-y_3),(z_1-z_3)$

[a] Centrosymmetrically related vectors are not listed.

[b] (x_1,y_1,z_1), (x_2,y_2,z_2), (x_3,y_3,z_3), and (x_4,y_4,z_4) are the coordinates of the Re1, Re2, Si1 and Si2 atoms respectively.

[c] Expected Peak Heights calculated as in Chapter II.

Re_1-Re_2, 444; 2Re, 222; Re-Si, 166.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson[73,74] map was computed between the limits $-0.5 \le u \le 0.5$, $-0.5 \le v \le 0.5$, and $0.0 \le w \le 0.5$. The rhenium-rhenium vectors were readily identified in the Patterson map and a consistent solution for the coordinates of the two independent rhenium atoms was found to be: Re1, (0.185, 0.363, 0.287) and Re2, (0.018, 0.163, 0.207). Image seeking around the origin and Re-Re vectors provided consistent solutions for the silicon atom coordinates as: Si1, (-0.069, 0.313, 0.142), and Si2, (0.275, 0.213, 0.357). The major vectors and their assignments are shown in Table 8.

A resumé of the refinement is shown in Table 9.

TABLE 9: REFINEMENT OUTLINE

	MODEL	R_1	R_2
1)	Rhenium and Silicon atoms isotropic	0.166	0.238
2)	All non-hydrogen atoms isotropic	0.106	0.131
3)	Decomposition and Absorption Corrections	0.061	0.078
4)	Re and Si anisotropic temperature factors	0.047	0.064
5)	All non-hydrogen atoms with anisotropic temperature factors	0.040	0.057

Structure factors were calculated using the atomic scattering factors[75] for the neutral atoms for rhenium, silicon, carbon, and oxygen. The real and imaginary parts of anomalous dispersion corrections[76] were applied to the rhenium and silicon scattering factors.[77] All non-hydrogen atoms were located from an electron density difference map phased on model 1 . Refinement of the model with all temperature factors anisotropic was suggested by features on an electron density difference map phased on model 4 , and was verified by a Hamilton's R Test[79] at the 0.005 significance level. Anisotropic temperature factors were of the form:

$$\exp\,[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)].$$

In an attempt to locate the hydrogen atoms an electron density difference map was calculated, phased on model 5 . The highest features were of the approximate magnitude 1.1e $\mathring{A}^{-3}$ and were located in the vicinity of the rhenium atoms, but could not be interpreted as hydrogen atom peaks. Similarly no peaks were observed in the positions predicted for the methylene hydrogens of the ethyl groups. The inability to locate hydrogens in this structure is due to similar problems as encountered for $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

The scattering is dominated too much by the heavy rhenium atoms and hampers location of the hydrogens. Also, it is probable that residual absorption effects severely limit the data. This is especially true in this structure due to the wide range of transmission factors.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 10. Table 11 contains the final fractional coordinates of all atoms except hydrogen, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters[80] (U's) and equivalent isotropic B's[81] of all atoms are shown in Table 12 and bond lengths and angles are given in Tables 13 and 14 respectively. The bond lengths and angles along with their standard deviations were obtained from ORFFE. Fig. 5 shows a three dimensional representation of the molecule. Least squares plane calculations are shown for the Re_2Si_2 plane (Table 15) showing the deviations of the Re and Si atoms from the plane and also the distances of the carbonyl groups, C2O2, C3O3 and C6O6, from this plane. Also the plane through the four carbonyl groups perpendicular to the Re_2Si_2 plane is calculated and also selected atom distances from this plane.

TABLE 10: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

[illegible]

Table 10 (continued)

K	L	FOBS	FCAL
H = 2*			
-2	-5	317	335
-2	-3	1200	1168
-2	-2	812	783
-2	-1	1620	1521
-2	0	595	610
-2	1	2557	2500
-2	2	546	553
-2	3	1011	1051
-2	4	303	290
-2	5	761	767
-2	6	150	126
-2	7	181	182
-2	9	505	510
-1	-6	425	390
-1	-5	313	300
-1	-4	1637	1670
-1	-3	786	785
-1	-2	3000	2965
-1	-1	561	537
-1	0	1350	1465
-1	1	124	103
-1	2	1395	1375
-1	3	213	206
-1	4	197	190
-1	6	281	282
-1	7	159	170
-1	8	722	705
0	-7	438	427
0	-6	350	365
0	-5	1610	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

Table 10 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 11: FRACTIONAL COORDINATES

Atom	x	y	z
Re1	0.02212(8)	0.16212(5)	0.20948(7)
Re2	0.19138(8)	0.35578(5)	0.29300(7)
Si1	0.2768(5)	0.1950(3)	0.3623(5)
Si2	-0.0608(5)	0.3230(3)	0.1359(5)
C1	0.143(2)	0.141(1)	0.040(2)
C2	-0.166(2)	0.123(1)	0.093(2)
C3	0.054(2)	0.037(1)	0.266(2)
C4	-0.092(2)	0.187(1)	0.381(2)
C5	0.309(2)	0.342(1)	0.117(2)
C6	0.303(2)	0.479(2)	0.351(2)
C7	0.078(2)	0.378(1)	0.470(2)
C8	0.460(2)	0.147(1)	0.284(2)
C9	0.273(2)	0.172(1)	0.560(2)
C10	0.479(2)	0.040(1)	0.287(2)
C11	0.426(2)	0.216(2)	0.650(2)
C12	-0.057(2)	0.342(1)	-0.061(2)
C13	-0.242(2)	0.369(1)	0.208(2)
C14	-0.198(2)	0.292(2)	-0.157(2)
C15	-0.288(2)	0.469(2)	0.169(2)
O1	0.212(2)	0.130(1)	-0.059(1)
O2	-0.281(2)	0.097(1)	0.027(1)
O3	0.081(2)	-0.041(1)	0.293(2)
O4	-0.164(2)	0.199(1)	0.482(1)
O5	0.378(1)	0.336(1)	0.019(1)
O6	0.362(2)	0.550(1)	0.393(2)
O7	0.015(2)	0.394(1)	0.574(1)

TABLE 12: THERMAL PARAMETERS (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B(Å^2)^a
Re1	0.0497(5)	0.0456(5)	0.0432(5)	-0.0010(4)	-0.0004(3)	0.0031(4)	3.67
Re2	0.0448(5)	0.0436(5)	0.0483(4)	0.0010(4)	-0.0038(4)	0.0039(4)	3.63
Si1	0.0585(30)	0.0501(26)	0.0519(26)	0.0069(23)	-0.00[illegible]2(21)	0.0098(21)	4.22
Si2	0.0512(28)	0.0553(27)	0.0483(25)	-0.0024(23)	-0.0051(21)	0.0101(21)	4.09
C1	0.070(13)	0.058(11)	0.071(14)	0.003(10)	0.014(11)	-0.013(11)	5.33
C2	0.076(13)	0.056(10)	0.040(10)	-0.017(9)	0.005(9)	-0.012(8)	4.68
C3	0.087(14)	0.053(11)	0.051(11)	-0.017(10)	-0.020(10)	0.008(9)	5.13
C4	0.055(12)	0.060(11)	0.059(13)	0.009(9)	0.006(10)	0.001(10)	4.58
C5	0.050(10)	0.054(10)	0.051(9)	-0.008(8)	-0.005(8)	0.014(8)	4.08
C6	0.038(10)	0.096(15)	0.067(12)	0.001(10)	-0.014(8)	0.001(11)	5.39
C7	0.074(12)	0.051(11)	0.052(10)	0.003(9)	-0.001(9)	0.006(8)	4.68
C8	0.057(12)	0.075(12)	0.082(14)	0.021(10)	0.012(10)	0.019(10)	5.50
C9	0.083(13)	0.077(12)	0.044(10)	-0.004(11)	-0.010(9)	0.015(9)	5.40

TABLE 12 CONTINUED

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B(\mathring{A}^2)^a$
C10	0.091(15)	0.065(13)	0.111(15)	0.027(11)	0.011(12)	0.025(12)	6.88
C11	0.092(15)	0.111(17)	0.069(13)	-0.014(13)	-0.033(11)	0.019(12)	7.28
C12	0.091(14)	0.067(12)	0.049(10)	-0.012(11)	-0.003(9)	0.008(8)	5.50
C13	0.054(11)	0.065(12)	0.089(13)	0.011(9)	0.000(9)	0.008(10)	5.48
C14	0.095(15)	0.101(15)	0.057(11)	-0.026(13)	-0.023(10)	0.019(11)	6.75
C15	0.066(13)	0.060(12)	0.115(16)	0.021(10)	0.004(11)	-0.000(11)	6.38
O1	0.111(12)	0.099(11)	0.074(10)	-0.009(9)	0.033(9)	-0.012(8)	7.52
O2	0.084(10)	0.093(10)	0.074(9)	-0.015(9)	-0.009(8)	-0.011(8)	6.79
O3	0.124(13)	0.063(9)	0.120(11)	0.007(9)	-0.006(9)	0.021(8)	8.06
O4	0.089(11)	0.107(11)	0.060(9)	-0.013(9)	0.008(8)	0.011(8)	6.75
O5	0.070(9)	0.101(10)	0.078(9)	0.007(8)	0.021(7)	0.010(8)	6.48
O6	0.087(11)	0.069(9)	0.124(12)	-0.020(8)	-0.024(9)	-0.002(9)	7.61
O7	0.108(11)	0.085(10)	0.076(9)	0.012(9)	0.031(8)	-0.018(7)	7.15

[a] Equivalent isotropic thermal parameter.

TABLE 13: INTRAMOLECULAR DISTANCES[a] (Å)

Atoms	Distance	Atoms	Distance
Re1-Re2	3.052(1)	Re2-Si1	2.539(4)
Re1-Si1	2.547(5)	Re2-Si2	2.549(4)
Re1-Si2	2.548(5)	Re1-C1	1.96(2)
Re1-C2	1.93(2)	Re1-C3	1.92(2)
Re1-C4	1.94(2)	Re2-C5	1.98(2)
Re2-C6	1.97(2)	Re2-C7	1.98(2)
C1-O1	1.13(2)	C2-O2	1.15(2)
C3-O3	1.18(2)	C4-O4	1.16(2)
C5-O5	1.12(2)	C6-O6	1.12(2)
C7-O7	1.15(2)	Si1-C8	1.90(2)
Si1-C9	1.91(2)	Si2-C12	1.89(2)
Si2-C13	1.85(2)	C9-C11	1.59(2)
C8-C10	1.53(2)	C12-C14	1.56(2)
C13-C15	1.54(2)		

[a] Standard deviations in parentheses refer to last digit quoted.

TABLE 14: INTRAMOLECULAR ANGLES (DEGREES)

Atoms	Angle	Atoms	Angle
Si1-Re2-Re1	53.3(1)	Si1-Re1-Re2	53.0(1)
Si2-Re2-Re1	53.2(1)	Si2-Re1-Re2	53.2(1)
Re2-Si1-Re1	73.7(1)	Re2-Si2-Re1	73.5(1)
Si1-Re1-C3	80.4(5)	Si2-Re1-C2	79.8(5)
Re2-Re1-C1	89.7(5)	Re2-Re1-C4	88.2(5)
Re1-Re2-C5	92.4(5)	Re1-Re2-C6	178.6(5)
Re1-Re2-C7	91.1(5)	Re1-C1-O1	179(2)
Re1-C2-O2	178(2)	Re1-C3-O3	175(2)
Re1-C4-O4	178(2)	Re2-C5-O5	178(2)
Re2-C6-O6	175(2)	Re2-C7-O7	178(2)
C8-Si1-C9	110.4(8)	C12-Si2-C13	109.6(8)
C10-C8-Si1	115(1)	C11-C9-Si1	110(1)
C14-C12-Si2	114(1)	C15-C13-Si2	116(1)
Si1-Re2-C6	125.5(5)	Si2-Re2-C6	128.0(5)

TABLE 15: LEAST SQUARES PLANE CALCULATIONS [a]
FOR $Re_2(CO)_7H_2(SiEt_2)_2$

(A) ATOMS DEFINING PLANE: Re1, Re2, Si1, Si2

EQUATION OF PLANE:

$$-0.5693X + 0.0653Y + 0.8195Z - 1.6898 = 0.0$$

DISTANCES OF ATOMS FROM PLANE:

		Re1	0.0029
		Re2	0.0031
Si1	-0.020	Si2	-0.020
C6	0.026	O6	0.127
C2	-0.017	O2	0.002
C3	0.179	O3	0.184
C5	-1.980		

(B) ATOMS DEFINING PLANE: Re1, Re2, C1, C4, C5, C7.

EQUATION OF PLANE:

$$0.6782X - 0.5229Y + 0.5163Z + 0.0354 = 0.0$$

DISTANCES OF ATOMS FROM PLANE:

Re1	0.0004	Re2	0.0004
C1	0.049	C4	-0.029
C5	-0.049	C7	0.016
O1	0.065	O4	-0.055
O5	-0.077	O7	0.038
C6	0.043	O6	0.089
Si1	-2.041		

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[a] X, Y, and Z are orthogonal coordinates (Å) with X along the *a*-axis, Y in the (*a*,*b*) plane, and Z along the *c**-axis.

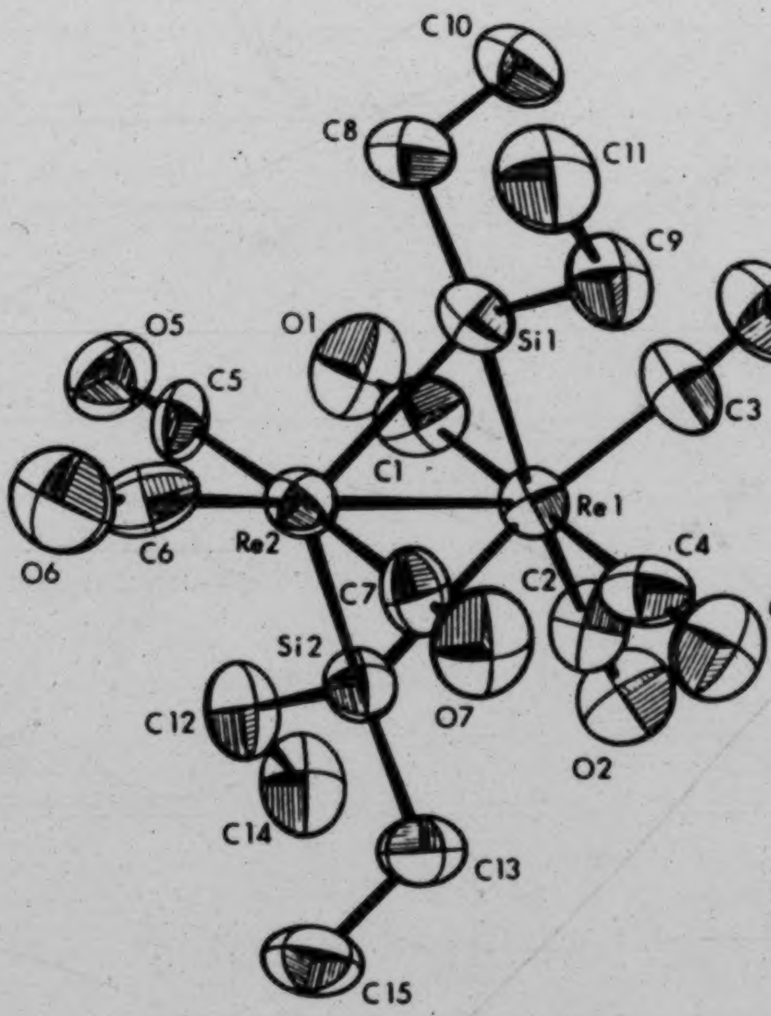

C10
C8
C11
C9
O5
O1
Si1
O3
C5
C3
C1
Re1
O6
C6
Re2
C4
C2
C7
O4
Si2
C12
O7
O2
C14
C13
C15

Fig. 5: A PERSPECTIVE VIEW OF $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$.

DESCRIPTION OF STRUCTURE

$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ has approximate C_s symmetry. A perspective view of the molecule is shown in Fig. 5. The central cluster is similar to that of $Re_2(CO)_6H_4$-$[Si(C_2H_5)_2]_2$ shown in Chapter II. The two rhenium atoms and two silicon atoms are planar and located at the corners of a rhombus, with like atoms at opposing corners, and a rhenium-rhenium bond across the shorter diagonal. Two carbonyl groups (C303 and C202) on Rel are also approximately in this plane and *trans* to the Rel-Sil and Rel-Si2 bonds, while one carbonyl group (C606), also in this plane and bonded to Re2, lies along the Re-Re bond. The two remaining carbonyls on each rhenium are perpendicular to the Re_2Si_2 plane above and below the rhenium atoms.

The rhenium-carbon (carbonyl) and carbon-oxygen distances are regular and similar to those observed in $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and other rhenium carbonyl compounds.[64,65,82,83,87,88,89] The coordination around the silicon atoms is a distorted tetrahedron due to the small Rel-Si-Re2 angles. There are no unusual distances in the silicon-carbon (ethyl) or carbon-carbon (ethyl) bonds (compare Chapter II). The rhenium-rhenium distance [3.052(1) Å] is consistent with a rhenium-rhenium single bond,and this is further substantiated by the acute Re1-Si1-Re2 and Re1-Si2-Re2 angles of 73.7(1)° and 73.5(1)°. It is also interesting that there is a progression in Re-Re bond lengths through the series $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_8H_2Si(C_6H_5)_2$,[65] whereas the Re-Si bonds are approximately constant (Table 16).

The longer Re-Re bond in $Re_2(CO)_8H_2Si(C_6H_5)_2$ reflects the fact that only one Si bridge is constraining the rhenium atoms together and also that the two extra eclipsed carbonyls are present causing added repulsion of the two $Re(CO)_4$ moieties. It is believed however that the Re-Re bond length differences in the other three compounds indicate that there is significant π bonding present in the Re-Re bonds whereas the Re-Si bonds are primarily σ. Thus varying the number of π-withdrawing carbonyl groups in the molecules would be expected to affect the Re-Re bonds if π bonding is important, but have little effect on the Re-Si bonds if the π bonding contribution here is not great.

Using the covalent radii of Pauling[27] for Si (1.17 Å) and Re (1.283 Å) a single bonded Re-Si distance of 2.45 Å is predicted, which is less than the observed value of approximately 2.54 Å in these compounds (Table 16). Although the radius used for rhenium may not be suitable, the larger observed Re-Si bond length does not weaken the argument that rhenium-silicon π bonding is of little significance in these compounds. A similar trend was observed[90] in $Cl(\pi C_5H_5)_2ZrSi(C_6H_5)_3$ where the observed Zr-Si distance [2.813(2) Å] exceeded the value calculated with Pauling radii (2.62 Å). Here Zr(IV) is formally d° so no back-donation into empty silicon d orbitals can occur. Thus it was postulated that only σ bonding was important. This contrasts with $Co(SiCl_3)(CO)_4$[91] and $RhHCl(SiCl_3)(PPh_3)_2$,[92] where the Co-Si [2.254(3) Å] and Rh-Si [2.303(4) Å] distances are both less than the values predicted using Pauling's covalent radii (2.33 Å and 2.42 Å respectively). It seems therefore that metal-silicon π bonding is present in these two compounds, whereas it is minimal in the zirconium and rhenium compounds. Any explanation of bond shortening as due to π bonding in these transition metal silyl compounds should be approached cautiously, however, since it is difficult to separate these effects from a σ-inductive effect. Thus the changes in metal-silicon distances in the series $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_6H_5)_3$,[93] [2.424(2) Å]; $(\pi\text{-}C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$,[94] [2.310(2) Å]; and also the series $Co(SiH_3)(CO)_4$,[95], [2.381(7) Å]; $Co(SiCl_3)(CO)_4$,[91] [2.254(3) Å]; and $Co(SiF_3)(CO)_4$,[96] [2.226(5) Å]; can be attributed to shrinkage of the silicon orbitals by the more electronegative substituents, thereby shortening the metal-silicon bonds.

However uncertain the mode of bonding between the rhenium and silicon atoms, it is still possible to compare the distances within the series mentioned in Chapter II since all substituents are similar. Thus the most interesting feature of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ is the similarity in the Re-Si bond lengths and their similarity to the other members of the series. The Re2-Si1 and Re2-Si2 bonds are adjacent to the hydrogen ligands whereas the Re1-Si1 and Re1-Si2 bonds are "hydrogen-free". As was explained in Chapter II, the similarity of these bonds in the two differing environments is not expected in view of the proposed hydrogen bridging.[62,63] Again, complete discussion of this phenomenon is deferred until Chapter IV.

CHAPTER IV: MODE OF BONDING OF THE HYDRIDE LIGANDS IN $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ AND $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$

Although location of the hydrogen atoms in this series of hydrides was not possible due to high dominance of the rhenium and tungsten scattering and also large absorption effects, investigation of the central framework, in particular the transition metal-silicon bond, has proved exceedingly valuable in obtaining information about the bonding exhibited by the hydrogens attached to the metals.[66] Three possibilities exist for the hydrogen bonding in these compounds as shown for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ in Fig. 6: (1) the hydrogen is terminally bonded to the transition metal with no interaction with the silicon, (2) the hydrogen bridges the transition metal-silicon bond thus forming a three centre two electron bond, and (3) the hydrogen is terminally bonded to the transition metal, but with weak attractive interaction with the silicon. A hydrogen bridge of type (2) was postulated[66] for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ in which the W-Si distances differed significantly (Table 16), with the hydrogen presumably bridging the longer distance. However,

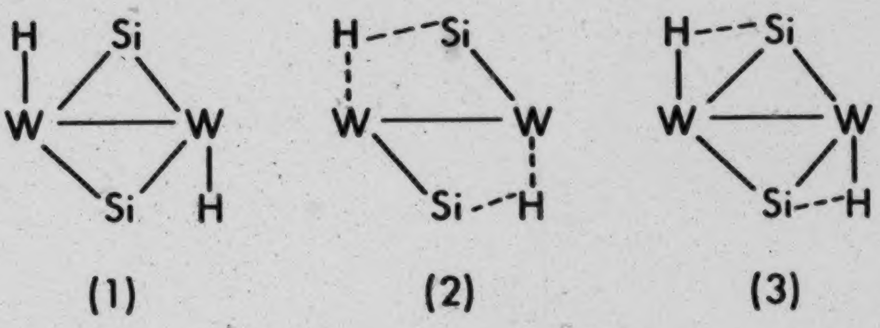


Fig. 6: Possible Bonding Schemes for the Hydrogen Ligand in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$.

in $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ the Re-Si bond lengths are not consistent with a three centre Si-H-Re bond, but rather seem consistent with a terminally bound hydrogen ligand.

It was expected that if the hydrogen was involved in a three centre Si-H-Re bond, a significant lengthening of this Si-Re distance would be observed, analogous to $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$. There is no significant difference in Re-Si bond lengths, however, between the two hydrides $Re_2(CO)_8H_2Si(C_6H_5)_2$[65] and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$, and $Re_2(CO)_8[Si(C_6H_5)_2]_2$[64] which contains no hydrogen ligand. Moreover these Re-Si distances are similar to the shorter (unbridged) W-Si distance in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, and therefore

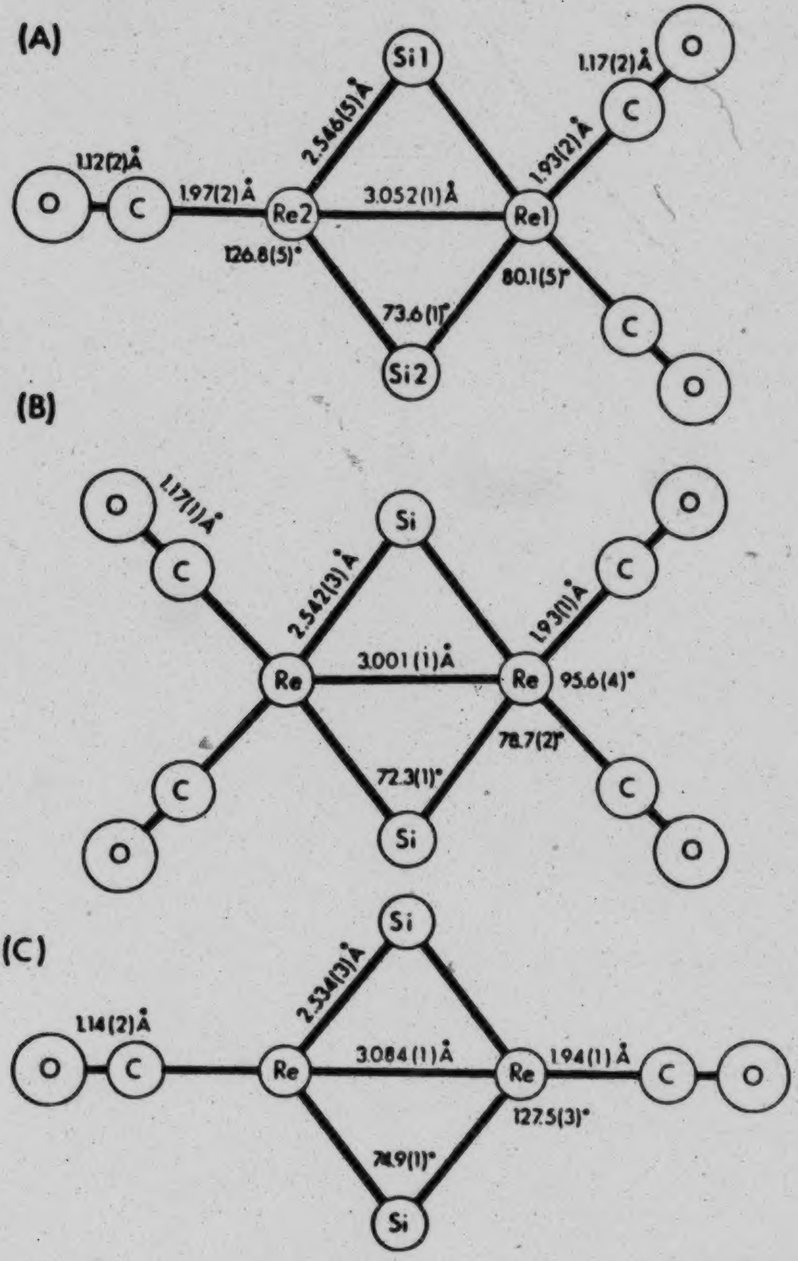
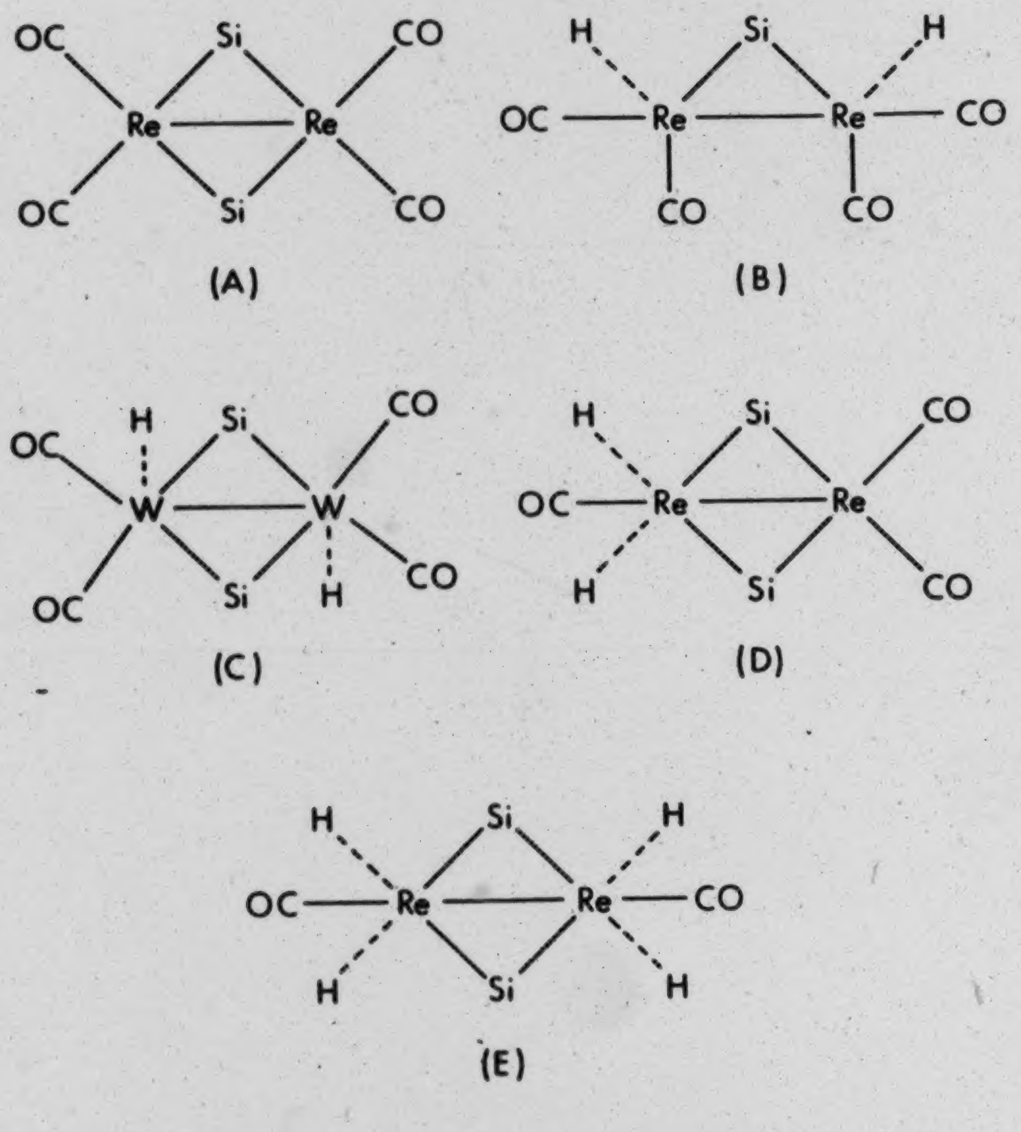

(A)
Si1
1.17(2)Å
O
C
2.546(5)Å
1.93(2)Å
1.12(2)Å
1.97(2)Å
3.052(1)Å
O
C
Re2
Re1
126.8(5)°
80.1(5)°
73.6(1)°
C
Si2
O
(B)
O
1.17(1)Å
O
Si
C
C
2.542(3)Å
1.93(1)Å
3.001(1)Å
Re
Re
95.6(4)°
78.7(2)°
72.3(1)°
C
C
Si
O
O
Si
(C)
2.534(3)Å
1.14(2)Å
3.084(1)Å
1.94(1)Å
O
C
Re
Re
C
O
127.5(3)°
74.9(1)°
Si

Fig. 7: A COMPARISON OF THE GEOMETRIES OF (A) $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, (B) $Re_2(CO)_8[Si(C_6H_5)_2]_2$, AND (C) $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

are more consistent with terminal hydrides.

The ambiguity in comparison of the Re-Si bond lengths in the hydrides and $Re_2(CO)_8[Si(C_6H_5)_2]_2$, in which the disorder problem existed (Appendix 1), was overcome with the structural determination of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, which, like the tungsten complex, was an internal standard containing metal-silicon bonds both adjacent to hydrogen ligands and "hydrogen-free". The similarity of the Re-Si bonds in this structure was added proof that the hydrogen ligands were not bonded in a fashion analogous to $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ and were therefore probably bound terminally to the rhenium atom. This reinforced the previous argument that the other rhenium hydrides in this series were also terminal. Fig. 7 shows $Re_2(CO)_8[Si(C_6H_5)_2]_2$, $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ viewed perpendicular to the Re_2Si_2 planes and including only those atoms lying approximately in this plane. Included are relevant bond lengths and angles for ready comparison of the three.

To explain why the hydrogen ligands seem to be terminally bound for the rhenium compounds, but bridging in the case of the tungsten compound, it is useful to consider the coordination about the metal atoms, as shown in Fig. 8. In each compound there are two mutually *trans* carbonyl groups on each metal which are not shown. These are perpendicular to the



(A) (B) (C) (D) (E)

Fig. 8: HYDROGEN LIGAND ENVIRONMENTS IN THE SILICON BRIDGED TRANSITION METAL HYDRIDES.

TABLE 16: RELEVANT BOND LENGTHS (Å) IN SOME TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	M-Si	M-M	REFERENCE
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	2.586(5), 2.703(4)	3.183(1)	66
$Re_2(CO)_8H_2Si(C_6H_5)_2$	2.544(9)	3.121(2)	65
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	2.542(3)	3.001(1)	64
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	2.533(2), 2.535(3)	3.084(1)	THIS WORK
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	2.547(5), 2.548(5) 2.539(4), 2.549(4)	3.052(1)	THIS WORK

TABLE 17: RELEVANT ANGLES (DEGREES) IN SOME TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	Si-M-M	M-Si-M	Si-M-C
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	53.02(10)	73.97(12)	109.1(5)
$Re_2(CO)_8H_2Si(C_6H_5)_2$	53.9(1)	72.3(1)	124.8(13)
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	52.2(2)	75.7(3)	78.7(2)
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	52.6(1)	74.9(1)	127.5(3)
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	53.2(1)	73.6(1)	126.8(5)

plane of the central cluster and are a constant feature of all the structures. Hydrogen atoms, although not located experimentally, are positioned in what are thought to be their approximate locations.

Viewing the hydrogen ligand environments in the examples shown, it is obvious that in the tungsten hydride (C), the hydrogen is more crowded than in the rhenium hydrides. The Si-W-C (carbonyl) angle, which encloses the hydrogen ligand is 109.1(5)° in the tungsten hydride, compared to the analogous angles of 124.8(13)°, 126.8(5)°, and 127.5(3)° in the rhenium hydrides (B), (D), and (E) respectively. It has been shown[93,94,97] that a normal non-bonded H-C (carbonyl) contact can be as low as 2.0 Å. For a Re-H distance[29] of 1.68 Å calculations show that in the rhenium hydrides, maintaining the minimum C-H contact, a H-Si contact of greater than 2.2 Å arises. However the situation is much different for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$. If no hydrogen bridging concept is utilized, then using the unbridged W-Si distance of 2.586 Å, and maintaining the minimum C-H contact, a very short Si-H contact of 1.72 Å occurs (this calculated assuming a W-H distance[98] of 1.70 Å). Even using the larger W-Si distance, a short Si-H contact of 1.81 Å arises. Therefore the hydrogen ligands are constrained to be considerably closer to the silicon atoms in the tungsten compound. It is believed that the crowding of the hydrogen by the carbonyl group is then responsible for the appearance of the three centre W-H-Si bond, since it is possible that the three centre bond is favoured energetically over a terminal hydride involving the high repulsion energy which must be associated with the very short Si-H non-bonded contacts mentioned.

The non-bonded Si-H contact of 2.2 Å calculated for the rhenium hydrides is believed to be reasonable. In $(\pi\text{-}C_5H_5)(CO)HFe(SiF_3)_2$ the hydrogen was not believed[99] bonded to either silicon atom and was located at 2.06(7) Å from both silicons. Although seemingly short, these non-bonded contacts can occur because in these systems the hydrogens approach the silicon atoms in electron density nodes, for example between the F-Si-F covalent bonds in $(\pi\text{-}C_5H_5)(CO)HFe(SiF_3)_2$, or between the C-Si-C bonds in the rhenium hydrides discussed. The repulsion is minimized in these bonding nodes thus facilitating the approach of the hydrogen ligand to the silicon atom.

There seems therefore to be no inherent stability of the hydrogen-bridged metal-silicon bond. Rather, the three centre bond is the result of steric crowding by an adjacent carbonyl group and only appears, as for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, when the hydrogen ligand is restricted to be close to the silicon atom.

Although evidence obtained from the structural investigations of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ combined with that obtained from[64,66] $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ and $Re(CO)_8[Si(C_2H_5)_2]_2$ exclude the possibility of a three centre Re-H-Si bond, it does not exclude the existence of weak attractive interaction of the hydrogen ligand with the silicon atom. An insight into this possibility is gained from the structural investigations[93,94,97] of $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_6H_5)_3$, $(\pi\text{-}C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$ and $(CO)_4FeHSi(C_6H_5)_3$, in which the hydrogen ligands were located experimentally. In both manganese compounds the hydrogens were located at 1.55(4) Å and 1.49(6) Å respectively from the manganese atoms and 1.76(4) Å and 1.79(6) Å respectively from the silicon atoms. However, in the iron compound the hydrogen atom was 1.64(10) Å from the iron atom and 2.73(10) Å from the silicon atom. In the two manganese hydrides the hydrogen ligands are constrained to be close to the silicon atoms due to steric crowding, the hydrogen being only 2.08(4) Å from the carbonyl in $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_6H_5)_3$ and 1.98(6) Å from the carbonyl in (π-C_5H_5)(CO)$_2$HMnSiCl$_2$(C_6H_5). There is no possibility of increasing the H-Si distance without increasing the hydrogen contact with the carbonyl groups. However in (CO)$_4$FeHSi(C_6H_5)$_3$ the hydrogen is not constrained to be close to the silicon atom, since it is in a sterically less crowded environment than the manganese hydrides. Thus the long Si-H contact observed is indicative of a terminally bound hydrogen with no attraction to the silicon atom. This is interpreted as meaning that there is no inherent stability of the weakly bridged hydrogen in this series in preference to a simple terminal hydrogen.

Thus in conclusion, in this series of transition metal hydrides, the hydrogen atoms are bound terminally to the transition metals in all the rhenium complexes. The hydrogens only approach the silicon atoms, as in the tungsten and manganese complexes, as a result of steric crowding and not as a result of any unusual attraction to the silicon atoms.

CHAPTER V: DITHIOLENE[100] INTRODUCTION

Interest in the bidentate dithiolene ligands began in the mid 1930's when R. E. D. Clark discovered[101,102] that toluene-3,4-dithiol and 1-chlorobenzene-3,4-dithiol reacted with zinc, cadmium, mercury and tin halides to form complexes of the type $[M(dithiol)_2]$. This reaction was found to be especially effective in the analytical determination of tin[103,104] and of molybdenum and tungsten[105,106,107] and most attention was directed towards this end. By the early 1960's several dithiolene complexes had been characterized[108,109,110] and were found to be of the form $M(dithiol)_2$ involving a variety of dithiolene ligands combined with nickel, cobalt, palladium, and molybdenum. These *bis* dithiol complexes were found to possess two unusual properties. Firstly, they exhibited the unusual square planar geometry[111,112,113,114] with the sulfur atoms in an almost perfect square about the metal. And secondly, they underwent facile reversible oxidation-reduction reactions[115] without changes in coordination geometry. The oxidized and reduced species were found to be related simply by one electron transfers and could be detected using polarography and voltammetry.

Attempts to produce the *bis* complexes of $S_2C_2Ph_2$ with V, Cr, Mo, Re, W, Ru, and Os[116] instead yielded the six coordinate *tris* complexes[117,118,119] which were similar to the *bis* complexes in that they also underwent the facile oxidation-reduction reactions.[119,120,121] The discovery[122] that $Co[S_2C_2(CN)_2]_2^-$ reversibly added one mole of ligand to form the complex $Co[S_2C_2(CN)_2]_3^{3-}$ led to the interesting suggestion that the six coordinate cobalt complex and possibly even the other *tris* complexes could be trigonal prismatic. In addition doubt about the octahedral coordination of these complexes was raised because of the inability to separate $Co[S_2C_2(CN)_2]_3^{3-}$ and $Mo[S_2C_2(CF_3)_2]_3$ into their optical enantiomers.[123] The possibility of trigonal prismatic coordination was extremely unusual since no six coordinate molecular complexes had been observed with non-octahedral coordination. Trigonal prismatic coordination *had* been observed[125] as early as 1923 in the compounds MoS_2 and WS_2 and later[126] in NiAs. However these were infinitely extended lattices and molecular packing was believed responsible for their unusual coordination.[124] It is noteworthy that on the basis of "directed valence" calculations, it had even been predicted by Hultgren[127] in 1932, that the only stable six coordinate complexes were trigonal prismatic and octahedral, the former being preferred for low lying d orbitals and the latter being preferred for higher energy d orbitals. In addition octahedral coordination would be favoured by increasing ionic character in the metal-ligand bonds and by the bulkiness of large ligands.

The existence of trigonal prismatic coordination in a molecular complex was not observed until 1965 when the X-ray structure determination[128,129] of $Re[S_2C_2(C_6H_5)_2]_3$ was completed. The subsequent structural determinations of $Mo(S_2C_2H_2)_3$[130] and $V[S_2C_2(C_6H_5)_2]_3$[131,132] also showed trigonal prismatic geometry and verified that the rhenium compound was not an isolated example but only one of a possible series of trigonal prismatic structures. In all three compounds the metals were surrounded by six sulfur atoms at the corners of a trigonal prism, with the dithiolene ligands radiating from the metals in a "paddle-wheel" arrangement. There was also a striking similarity in the prism dimensions of the three compounds (Table 48). The intra- and interligand sulfur-sulfur distances are similar in all cases with the approximate values 3.06 Å and 3.08 Å respectively. The shortness of these "non-bonded" contacts led to the speculation that some sulfur-sulfur bonding was involved[124] in stabilizing the trigonal prism. Another remarkable feature of the three complexes was the similarity in the metal-sulfur bond lengths, averaging 2.33 Å, despite the fact that the covalent and ionic radii[133] of vanadium differed from those of molybdenum and rhenium by 0.07 Å. This similarity was viewed as an added consequence of the interligand S-S bonding.[124] In addition the S-C distances, averaging 1.69 Å were found to be consistent with considerable double bond character as seen from a comparison with the S=C double bond in thiourea[134] $[SC(NH_2)_2]$ and its derivatives,[135] measuring 1.720 Å.

Slight differences are, however, present in the three compounds which lead to distortions from the idealized D_{3h} symmetry. $Re[S_2C_2(C_6H_5)_2]_3$ and $Mo[S_2C_2(CN)_2]_3$ both have approximate C_{3h} symmetry caused by twisting of the phenyl groups out of the ligand planes in the former and by a deviation of the S_2C_2 planes from the MS_2 planes by 18° in the latter. In $V[S_2C_2(C_6H_5)_2]_3$ the unique ligand on the crystallographic two-fold differs slightly from the other two, however the molecule still closely approximates D_{3h} symmetry.

Comparison of the electron spin resonance and electronic spectra in the solid state and in solution[136] confirmed that the trigonal prismatic coordination was also present in solution and therefore was a consequence of intramolecular phenomena rather than intermolecular effects. It was also apparent in all the electronic spectra that the dominant feature was an intense two-band pattern in the visible region,[137] the first at about 15,000 cm^{-1} ($\varepsilon \sim 25000$) and the second at about 24,000 cm^{-1} ($\varepsilon \sim 15000$). This was believed to be characteristic of all trigonal prismatic dithiolenes.

In an attempt to explain the stability of the trigonal prism over the octahedron, two separate molecular orbital treatments were presented. In the treatment by Schrauzer and Mayweg[138] no reason for the stability of the trigonal prism is obvious since calculations performed on a hypothetical octahedral complex $MS_6C_6R_6$ yielded the same orbital ordering as the trigonal prismatic calculations. Also objections based on electron spin resonance spectra have been raised[139] concerning the ordering of the highest occupied and lowest unoccupied levels for this scheme. The scheme by Gray *et. al.*,[137] which seems more consistent with electron spin resonance spectra, electronic spectra and polarographic work is therefore favoured in this work. Both schemes are discussed further in Chapter IX where a detailed explanation of the trigonal prism is given based on

Gray's molecular orbital calculations.

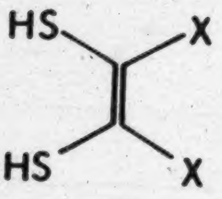
Although the neutral *tris* dithiolenes were found to be trigonal prismatic, subsequent structural determinations on $V[S_2C_2(CN)_2]_3^{2-}$,[142] $Mo[S_2C_2(CN)_2]_3^{2-}$,[141] and $Fe[S_2C_2(CN)_2]_3^{2-}$[142] showed coordinations which varied from highly distorted octahedrons for the vanadium and molybdenum dianions to an almost regular octahedral coordination for the iron dianion. Interligand sulfur-sulfur distances in the three were greater than for the neutral trigonal prisms and thus were consistent with a breakdown in the sulfur-sulfur bonding which had been proposed[124] as a stabilizing factor in the prism. In addition the extra electrons in the molybdenum dianion as compared to the neutral molybdenum complex were located in an orbital which was said to be antibonding in the trigonal prism[141] thus offering an explanation of the deviation from the trigonal prismatic coordination. The trend therefore emerged that the neutral *tris* 1,2-dithiolenes were trigonal prismatic whereas the dianions were octahedral or distorted octahedral. The reasons for the trigonal prismatic and octahedral coordination in these dithiolenes was not obvious however and little was published correlating the observed structures to the molecular orbital descriptions of either Gray or

Schrauzer.

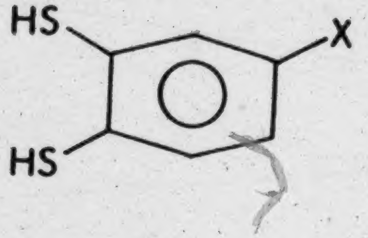
The compounds $Mo(S_2C_6H_4)_3$, $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$, and $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$, which form the subject matter for the remainder of this thesis, therefore constitute an interesting and potentially informative series. Firstly the $M(S_2C_6H_4)_3^{n-}$, (n = 0, 1, 2 for M = Mo, Nb, Zr, respectively), moeities form an isoelectronic series so that the only differences are in the central metal. From a molecular orbital viewpoint, this means only the d orbital energies vary throughout the series. Hence, the effect that varying the central metal, and thus the metal d orbitals, will have on the coordination of the metals can be observed, and hopefully correlated to Gray's molecular orbital description for trigonal prismatic geometry. Also since identical ligands ($S_2C_6H_4{}^{2-}$) are involved, subtle geometry changes involving angles and bond lengths can be more readily compared, than if differing ligands are used.

From a comparison of their electronic spectra[137,143] in Table 18 it is obvious that gross differences exist within the three compounds. For the molybdenum[137,144] and niobium[143] complexes the spectra were similar, both having absorptions which were believed characteristic of trigonal prismatic coordination.[137] The spectrum[143] of $Zr(S_2C_6H_4)_3^{2-}$ however, was found to be vastly different and was not indicative of a trigonal prism. Thus on the basis of the electronic spectral results it seems that varying the central metal from Mo to Nb to Zr causes changes in the coordination, presumably destabilizing the trigonal prism and favouring a tendency towards octahedral coordination as was observed in $Mo[S_2C_2(CN)_2]_3^{2-}$ and $V[S_2C_2(CN)_2]_3^{2-}$. It was believed that a complete structural determination of this series of *tris* 1,2-dithiolene complexes would prove useful in understanding further the factors which stabilize trigonal prismatic coordination. It was also of interest to discover whether the electronic spectra were reliable indicators of the coordination geometry in these compounds.

The common 1,2-dithiol ligands and their normal abbreviations, which will be used in this thesis, are shown below.



X = H dithioglyoxal
= CN maleonitrile-dithiol (mnt)
= C_6H_5 *cis* 1,2-diphenylethene-1,2-dithiol (sdt)



X = H benzene-1,2-dithiol (bdt)

= CH_3 toluene-3,4-dithiol (tdt)

TABLE 18: ELECTRONIC SPECTRA FOR MOLYBDENUM, NIOBIUM, AND ZIRCONIUM BENZENE DITHIOLS[137,143]

COMPLEX	COLOUR	BAND MAXIMA, cm^{-1} (ϵ in parentheses)
$Mo(S_2C_6H_4)_3$[144]	Dark Green	11,500 sh (1000); 14,463 (20,900); 22,990 (17,400).
$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$	Dark Purple	17,700 (10,700); 27,200 (13,800); 30,700 sh (9,120).
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$	Red	20,000 sh (2,030); 35,800 sh (25,200).

CHAPTER VI: THE CRYSTAL AND MOLECULAR STRUCTURE OF *TRIS* (BENZENE-1,2-DITHIOLATO) MOLYBDENUM, $[Mo(S_2C_6H_4)_3]$.

EXPERIMENTAL

Dark green crystals of $Mo(bdt)_3$ suitable for X-ray diffraction study, prepared by the reaction of molybdenum pentachloride with benzene dithiol,[137] were kindly supplied by Dr. Takats and Mr. Martin.[143] Preliminary photography revealed mmm Laué symmetry, indicating an orthorhombic space group. The systematic absences as determined from Weissenberg ($0k\ell$, $1k\ell$; CuK_α X-radiation) and Precession ($h0\ell$, $h1\ell$, $hk0$, hkl; MoK_α X-radiation) photographs are $0k\ell$: $k + \ell = 2n + 1$ and $h0\ell$: $h = 2n + 1$, consistent with the space groups Pnam and $Pna2_1$. Precise lattice parameters were obtained at 22°C from a least squares refinement of the setting angles of 12 reflections which were accurately centred on a Picker automatic four-circle diffractometer, using CuK_{α_1} X-radiation ($\lambda = 1.54051$ Å). The cell parameters and their standard deviations are: $a = 16.093(3)$ Å, $b = 10.177(1)$ Å, and $c = 11.906(2)$ Å.

The observed density, obtained by floatation in aqueous zinc bromide solution, is 1.74(2) g cm^{-3} and is in good agreement with the calculated value of 1.75 g cm^{-3}, obtained assuming four molecules of molecular weight 516.60 a.m.u. per unit cell of volume 1952.84 Å^{3}. For space group Pna2$_1$ there are 4 general equivalent positions and no restrictions are possible. However for Pnam there are 8 general equivalent positions so the molecules are restricted to lie either on the mirror planes or inversion centres. The *tris* chelate structure cannot have an inversion centre, hence for space group Pnam, the molecule must possess symmetry m.

Intensity data were collected on the Picker automatic four circle diffractometer using CuK$_\alpha$ X-radiation, filtered with 0.0005" thick nickel foil (in preference to a graphite monochromator[145]) and using a 2° take-off angle. The crystal was aligned in a general orientation but with its a^* axis approximately coincident with the diffractometer ϕ axis. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: $\{1,0,0\}$, 0.206 mm; $\{0,1,0\}$, 0.055 mm; $\{0,0,1\}$, 0.077 mm. A coupled $2\theta/\omega$ scan was used, with a 2θ scan speed, of 1°/min to collect all reflections with $2\theta \leq 125°$. The peak scan was approximately two minutes (2°), increasing as the $\alpha_1\alpha_2$ resolution increased. Stationary background counts of 40 secs. were collected on either side of the peak. Assuming approximate linearity of background, the intensities and standard deviations were calculated as shown previously in Chapter II. The detector was a scintillation counter and was used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition data collection was interrupted periodically to collect a further five standard reflections to investigate possible decomposition. No significant decomposition was observed over the duration of the data collection. Of the 1806 reflections collected, 1050 were significantly above background with $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. Terms used in the Zachariasen extinction correction were calculated at this stage. Standard deviations, $\sigma(F)$, in the structure factors were again computed using a "p factor"[70] of 0.03.

The linear absorption coefficient[86] using CuK_α radiation is 110.67 cm^{-1}, giving rise to a range of transmission factors between 0.5768 and 0.3099.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened 3-dimensional Patterson map[146] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. The Mo-Mo vectors for both $Pna2_1$ and Pnam (with the molybdenum atom on the crystallographic mirror) are shown in Table 19. It is obvious that the two space groups cannot be distinguished in the Patterson on the basis of the Mo-Mo vectors alone. However the molybdenum position was obtained as follows. The most intense peak was situated at (0.500, 0.0, 0.0) and was attributed to the vector (1/2, 1/2-2y, 0); thus the y coordinate was obtained as ± 0.25. The accidentally special y coordinate leads to an ambiguity in the assignment of the next most intense peaks, observed at (0.325, 0.500, 0.500) and (0.182, 0.500, 0.500), as vectors of the form (1/2-2x, 1/2, 1/2) and (2x, 2y, 1/2). Because of this failure to identify the true Harker line vector, two possible solutions for molybdenum coordinates had to be tested by subsequent structure factor calculations and least squares refinement. The solutions to be tested were (a) $x = 0.09$, $y = 0.25$, $z = 0.25$, and (b) $x = 0.16$, $y = 0.25$ and $z = 0.25$.

The fourth largest peak on the map, at (0.0, 0.0,

TABLE 19: HARKER VECTORS FOR Mo(bdt)$_3$

$Pna2_1$		Pnam (z=1/4), SPECIAL POSITION "C"	
VECTOR FORM	WEIGHT	VECTOR FORM	WEIGHT
1/2-2x,1/2,1/2	2	1/2-2x,1/2,1/2	2
1/2+2x,1/2,1/2	2	1/2+2x,1/2,1/2	2
1/2,1/2-2y,0	2	1/2,1/2-2y,0	2
1/2,1/2+2y,0	2	1/2,1/2+2y,0	2
2x,2y,1/2	1	2x,2y,1/2	1
-2x,-2y,1/2	1	-2x,-2y,1/2	1
2x,-2y,1/2	1	2x,-2y,1/2	1
-2x,2y,1/2	1	-2x,2y,1/2	1

0.255), was located at 3.04 Å from the origin and was consistent with a build-up of S-S vectors between sulfur atoms related by a mirror perpendicular to z. Since this was the largest S-S vector, the possibility of the mirror bisecting the triangular faces was excluded and the space group was probably Pnam with the mirror relating the two triangular faces of the trigonal prism. If this were the case, then Mo-S vectors should be observed at w coordinates of about 1/2(0.255) ≈ 0.13. Three vectors at 2.3 - 2.4 Å from the origin were located with w coordinates 0.136 and were consistent with the trigonal prismatic geometry. In addition three vectors were located in the w = 0 plane at 3.04 - 3.17 Å from the origin and these were consistent with vectors between the sulfur atoms within the triangular faces. From the Mo-S and S-S vectors the sulfur positions were calculated as either: S1(0.11, 0.14, 0.38), S2(0.16, 0.42, 0.38) and S3(0.29, 0.21, 0.38) corresponding to Mo position (b) or S1(0.04, 0.14, 0.38), S2(0.09, 0.42, 0.38) and S3(0.22, 0.21, 0.38) corresponding to Mo position (a).

To obtain the proper x coordinates a least squares refinement was performed with the model based on Mo positions (b). This model showed no signs of successful refinement and converged after two cycles to give $R_1 = 0.424$ and $R_2 = 0.516$. However the model based on Mo coordinates (a) refined to $R_1 = 0.349$ and $R_2 = 0.435$ in two cycles. Temperature factors were fixed in these cycles, so further refinement of the second model, varying the temperature factors yielded $R_1 = 0.209$ and $R_2 = 0.294$ after the three cycles and thus the model was assumed to be correct. An outline of the solution and refinement is shown in Table 20.

TABLE 20: REFINEMENT OUTLINE

	Model	R_1	R_2
(1)	Mo and S atoms based on Mo coordinates (0.16,0.25,0.25)	0.424	0.516
(2)	Mo and S atoms based on Mo coordinates (0.09,0.25,0.25)	0.349	0.435
(3)	Mo and S atoms of model (2) - varying temperature factors	0.209	0.294
(4)	Mo, S, and C atoms; isotropic B's	0.079	0.086
(5)	Absorption Correction	0.065	0.075
(6)	Mo and S atoms anisotropic	0.050	0.062
(7)	H positions added	0.046	0.051
(8)	Extinction correction[147]	0.042	0.042
(9)	Carbon atoms anisotropic	0.035	0.034

Structure factors were calculated using the atomic scattering factors of the neutral atoms for molybdenum, sulfur and carbon compiled by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] In addition anomalous dispersion corrections,[76] both real and imaginary, were applied to the molybdenum and sulfur scattering factors ($^{\Delta}f'_{Mo} = -0.54$, $^{\Delta}f''_{Mo} = 2.89$, $^{\Delta}f'_{S} = 0.31$, $^{\Delta}f''_{S} = 0.58$).

The carbon atoms were located from an electron density difference map phased on model (3). Anisotropic temperature factors for the different groups of atoms were introduced, as indicated by features in electron density difference maps, and can be justified, at the 0.005 significance level, by the subsequent application of Hamilton's R factor ratio test.[79] In the difference map, phased on model (6), the hydrogen atoms were visible so they were included in subsequent refinements, their positions calculated from the known geometry and orientation of the benzene rings, and using a C-H distance of 1.0 Å. The hydrogen atoms were assigned thermal parameters approximately 15% higher than those of the attached carbon atoms. Although they were included in the structure factor calculations, their parameters were not refined.

Extinction corrections[147] were applied since comparison of $|F_o|$ and $|F_c|$ for low angle reflections suggested the problem may exist. Verification of the importance of the extinction correction is evident in the results of the refinements before and after this correction. Before the correction, all reflections except one with sin $\theta/\lambda \leq 0.084$ were rejected from the refinement on the basis that $|\Delta F/\sigma(F)| > 5.0$, and in all cases $|F_o|$ was less than $|F_c|$ for these reflections. After the extinction correction, only one of these reflections previously rejected was still rejected from the refinement. The final refined value of the extinction scale factor, C, is 2.371×10^{-6}.

Anomalous features in the thermal parameters (*vide infra*) suggested that the scattering factors could be inadequate. Several refinements were attempted using various alternative scattering factors [Mo(IV),[150] Mo(VI),[150] S^- [75]] but no better agreement in R factor and no more reasonable thermal parameters were obtained. Thus the results from the original refinement are reported.

Programmes used in solution, refinement and presentation of data are listed in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 21. The final fractional coordinates of all atoms and their isotropic temperature factors are shown in Table 22, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters[80] (U_{ij}'s) of all anisotropic atoms are shown in Table 23. Relevant intramolecular bond lengths are shown in Table 24 and the intramolecular angles in Table 25. Intermolecular contacts which are close to the predicted van der Waals separations[151] are listed in Table 26. These bond lengths, intermolecular contacts and bond angles, along with their standard deviations were obtained from ORFFE (See Appendix 2). Several least squares plane calculations are shown in Table 27, along with the deviations of the atoms from the planes. In addition, Table 28 shows the dihedral angles between selected planes.

In the three dimensional drawings of the molecule, 50% probability thermal ellipsoids are shown for molybdenum and sulfur atoms. For the carbon atoms artificially low isotropic thermal parameters were used for clarity of the diagram. Similarly the hydrogen atoms were excluded from the plot for clarity. The hydrogen atoms are numbered from H1 to H6 and are bonded sequentially to the second and third carbon atoms in the rings. In the packing diagram in Fig. 13, the open bonds represent molecules at $z = 0.25$ whereas the dark bonds represent molecules at $z = 0.75$.

TABLE 21: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 0**				2	5	455	442	0	5	579	582	6	2	338	294	6	1	578	579
0	2	3512	3133	2	6	148	168	0	6	646	663	6	3	331	332	6	2	365	335
0	4	2258	2159	2	11	240	241	0	7	1625	1585	6	5	488	454	6	3	804	776
0	6	628	664	3	0	858	850	0	8	815	803	6	6	350	339	6	5	565	483
0	8	2010	1969	3	1	642	635	0	9	896	888	6	7	825	809	6	6	285	273
0	12	404	428	3	2	138	143	0	13	288	300	6	9	639	630	6	7	617	595
1	1	2346	2421	3	3	370	383	1	0	1800	1761	6	10	220	201	6	8	472	442
1	3	278	258	3	4	912	911	1	1	604	620	6	11	304	270	6	9	255	268
1	5	440	459	3	5	390	395	1	2	961	978	7	0	766	777	6	11	384	393
1	7	2098	2060	3	7	205	157	1	3	372	383	7	1	451	468	7	0	911	914
1	9	1115	1098	3	8	371	375	1	4	442	440	7	2	720	714	7	1	883	933
1	13	245	276	3	10	257	266	1	5	443	445	7	4	627	619	7	4	852	853
2	0	520	515	3	11	265	286	1	6	1153	1160	7	6	528	490	7	7	532	508
2	2	836	852	3	12	375	347	1	7	594	561	7	7	496	472	7	8	565	560
2	4	1147	1168	4	0	577	587	1	8	1205	1190	7	8	395	383	7	9	244	254
2	6	1371	1333	4	1	164	145	1	9	395	379	7	9	312	317	8	0	664	673
2	8	1089	1067	4	2	472	457	1	10	429	422	7	10	327	338	8	1	363	366
2	10	608	604	4	3	1447	1417	1	12	217	206	8	0	303	323	8	2	298	317
2	12	420	429	4	4	996	956	1	13	161	168	8	3	935	920	8	3	391	414
3	1	798	823	4	5	651	671	2	0	435	420	8	5	745	765	8	5	269	281
3	3	1888	1895	4	7	718	708	2	1	2428	2520	8	6	321	322	8	6	266	272
3	5	1397	1365	4	8	549	541	2	2	775	794	8	8	351	338	8	7	292	299
3	7	421	416	4	9	312	333	2	3	774	800	8	9	174	157	8	8	362	319
3	9	474	477	4	10	190	142	2	4	980	950	9	0	314	323	9	1	209	205
3	11	742	740	4	11	452	413	2	5	494	520	9	1	546	532	9	3	330	339
3	13	460	444	4	12	319	307	2	6	253	226	9	2	585	587	9	5	273	305
4	0	666	679	5	0	230	213	2	7	763	760	9	4	684	681	10	2	224	234
4	2	902	900	5	1	281	290	2	9	696	659	9	6	246	233	10	3	171	160
4	4	1148	1168	5	3	655	652	2	10	421	393	9	7	341	334	10	4	435	428
4	6	779	765	5	4	389	402	2	11	367	350	10	0	640	654	10	6	180	193
4	8	640	631	5	5	400	402	2	12	375	384	10	1	271	275	11	0	263	248
4	10	790	793	5	6	172	131	2	13	247	284	10	2	201	197	11	1	165	132
4	12	550	539	5	7	340	335	3	0	709	658	10	3	397	415	11	3	333	329
5	1	974	992	5	10	238	255	3	1	586	573	10	4	174	190	11	4	162	190
5	3	823	835	5	11	358	331	3	2	1079	1055	10	5	351	378	**H = 4****			
5	5	811	803	5	12	164	165	3	3	1578	1579	10	6	168	191	0	0	672	672
5	7	761	766	6	0	230	242	3	4	1266	1256	10	7	265	268	0	1	2502	2546
5	9	617	627	6	1	551	557	3	5	1119	1113	11	0	357	383	0	2	1074	1063
5	11	456	435	6	2	196	235	3	6	788	765	11	1	458	442	0	3	705	719
6	0	1262	1263	6	4	553	535	3	7	374	368	11	2	305	295	0	4	1255	1262
6	2	1248	1228	6	7	519	484	3	8	470	479	11	4	218	215	0	5	357	372
6	4	923	891	6	9	295	310	3	10	492	496	**H = 3****				0	6	319	311
6	6	568	544	7	0	1080	1110	3	11	634	656	1	1	1486	1493	0	7	630	635
6	8	331	303	7	2	206	193	3	12	431	437	1	3	623	619	0	9	591	610
6	10	184	233	7	3	239	268	3	13	306	296	1	5	532	515	0	10	508	504
7	1	902	888	7	4	525	501	4	0	665	656	1	7	325	320	0	11	366	334
7	3	785	786	7	5	207	195	4	1	882	874	1	9	214	125	0	12	500	515
7	5	611	600	7	6	347	314	4	2	703	666	1	11	301	286	0	13	257	239
7	7	440	430	7	8	687	668	4	3	1181	1175	2	0	1679	1671	1	0	275	242
7	9	383	388	8	1	370	363	4	4	1494	1476	2	1	258	258	1	1	456	459
8	2	411	392	8	4	259	304	4	5	925	922	2	2	628	624	1	2	593	637
8	4	749	765	8	7	408	434	4	6	211	188	2	4	388	401	1	3	1224	1240
8	6	565	585	8	9	172	215	4	7	597	567	2	8	188	225	1	4	1351	1297
8	8	464	457	9	2	275	279	4	8	378	382	3	0	276	275	1	5	1131	1142
8	10	504	515	9	3	222	282	4	9	475	443	3	4	207	171	1	6	853	888
9	1	583	583	9	4	533	525	4	10	347	325	3	5	256	241	1	7	231	235
9	3	656	648	9	5	284	299	4	11	411	422	3	7	201	211	1	8	542	529
9	5	461	463	10	3	588	661	4	12	506	566	4	0	571	555	1	9	242	270
9	7	280	267	10	4	320	300	5	0	1245	1225	4	2	177	176	1	10	556	568
10	0	227	256	10	5	388	397	5	1	341	356	4	4	652	670	1	11	559	582
10	2	381	380	10	7	168	173	5	2	840	827	4	6	245	214	1	12	462	481
10	4	485	479	11	0	164	76	5	3	659	657	4	10	299	200	1	13	265	317
10	6	368	391	11	1	175	177	5	4	487	476	4	12	225	214	2	0	449	443
11	1	395	407	11	2	240	241	5	5	483	467	5	0	711	702	2	2	792	798
11	3	263	297	11	3	180	193	5	6	741	729	5	4	551	532	2	3	1852	1908
H = 1**				11	4	443	457	5	8	813	778	5	7	428	403	2	4	946	937
1	0	128	157	**H = 2****				5	10	426	422	5	8	294	293	2	5	1444	1451
2	0	581	590	0	0	1296	1329	5	11	318	259	5	9	405	426	2	6	530	515
2	1	721	741	0	1	2124	2030	5	12	216	220	5	11	192	180	2	8	278	267
2	3	400	416	0	2	417	434	6	0	535	541	5	12	232	204	2	9	247	218
2	4	335	335	0	3	195	185	6	1	859	869	6	0	846	843				

Table 21 (continued)

K	L	FOBS	FCAL
H = 4**			
2	10	369	350
2	11	777	783
2	12	329	340
2	13	416	424
3	1	1205	1190
3	2	1503	1472
3	3	614	600
3	4	2093	2040
3	5	399	383
3	6	298	291
3	7	462	475
3	8	391	395
3	9	356	331
3	10	519	486
3	12	673	682
4	0	1485	1495
4	1	590	594
4	2	616	605
4	3	990	1000
4	5	781	783
4	6	460	468
4	7	306	298
4	8	719	734
4	9	446	451
4	10	234	232
4	11	558	568
5	0	723	730
5	1	928	921
5	2	424	441
5	4	329	353
5	5	265	236
5	6	756	756
5	7	742	733
5	8	824	807
5	9	413	440
5	10	409	414
5	12	175	200
6	0	575	577
6	1	915	937
6	2	465	444
6	3	386	395
6	4	351	321
6	5	400	411
6	6	431	449
6	7	665	675
6	8	421	402
6	9	352	360
7	0	888	881
7	1	330	313
7	2	563	565
7	3	386	396
7	4	288	295
7	5	398	391
7	6	483	466
7	7	325	300
7	8	453	459
7	9	277	274
7	10	220	223
8	1	358	340
8	2	254	265
8	3	395	435
8	4	563	554
8	5	484	456
8	6	311	295
8	7	388	375
8	9	295	303
9	0	710	722
9	1	291	295
9	2	532	538
9	3	496	515
9	4	237	280
9	5	308	327
9	6	239	230
9	8	228	255
10	1	379	420
10	2	229	257
10	4	380	355
10	5	175	153
10	6	177	176
11	0	569	571
11	1	224	258
11	2	159	177
11	3	179	187
H = 5**			
1	0	1106	1070
1	1	670	673
1	2	125	132
1	3	176	214
1	4	624	620
1	5	228	223
1	6	206	182
1	7	169	208
1	8	435	436
1	11	210	185
1	12	156	223
2	1	581	602
2	2	285	293
2	3	971	970
2	4	255	291
2	5	381	384
2	6	273	253
2	7	965	951
2	8	309	349
2	9	433	449
2	11	322	353
3	0	1563	1561
3	4	1085	1074
3	6	291	307
3	8	878	874
3	12	312	302
4	0	237	217
4	1	1109	1074
4	2	315	292
4	3	206	170
4	4	550	555
4	7	200	175
4	8	317	324
4	12	163	166
5	0	206	173
5	3	185	185
5	5	177	176
5	6	244	258
5	8	241	288
5	11	165	98
6	0	526	544
6	1	213	190
6	4	228	222
6	5	213	237
6	7	226	274
6	8	295	253
7	0	665	602
7	1	670	684
7	2	261	274
7	3	282	290
7	5	247	248
7	7	351	341
7	8	322	300
8	0	200	210
8	1	241	257
8	6	189	204
8	7	291	288
8	8	247	263
8	9	207	212
9	[illegible]	219	242
9	2	216	228
9	3	185	190
9	5	236	248
9	6	197	223
10	1	412	422
10	4	320	315
11	0	427	440
11	2	242	232
H = 6**			
0	0	1346	1359
0	1	542	554
0	2	1742	1693
0	3	1265	1274
0	4	1566	1540
0	5	728	753
0	6	521	533
0	7	645	659
0	9	257	263
0	10	479	470
0	11	458	506
0	12	541	564
1	0	949	914
1	1	474	476
1	2	245	265
1	3	1719	1733
1	4	1059	1057
1	5	1322	1316
1	7	320	299
1	8	420	427
1	9	361	346
1	10	251	226
1	11	707	693
1	12	352	362
2	0	683	677
2	2	1009	1042
2	3	318	328
2	4	1291	1296
2	5	275	252
2	6	641	647
2	8	434	431
2	10	719	746
2	12	554	568
3	0	173	192
3	1	342	346
3	2	1034	1072
3	5	1054	1060
3	6	229	220
3	7	644	654
3	8	243	240
3	9	634	613
3	11	572	589
4	0	941	953
4	1	227	220
4	2	797	795
4	4	625	631
4	6	805	793
4	8	781	773
4	10	442	440
4	12	227	270
5	1	1480	1458
5	2	218	175
5	3	300	273
5	4	317	318
5	5	330	256
5	7	988	940
5	9	601	608
5	10	177	87
6	0	1456	1486
6	2	796	783
6	3	245	261
6	4	201	161
6	5	223	196
6	6	580	573
6	8	701	666
6	10	195	214
7	0	284	267
7	1	805	803
7	3	589	585
7	5	526	500
7	7	450	442
7	9	324	314
8	0	219	167
8	1	236	231
8	2	401	409
8	4	902	910
8	6	496	483
8	7	293	270
9	0	356	348
9	1	260	257
9	3	636	640
9	4	205	180
9	5	508	521
10	0	308	305
10	2	324	339
10	4	359	358
11	1	513	523
H = 7**			
1	0	1099	1049
1	2	252	248
1	3	310	282
1	4	999	978
1	6	212	194
1	7	210	230
1	8	689	698
1	12	257	264
2	0	354	339
2	1	678	677
2	3	477	474
2	5	280	262
2	7	520	535
2	8	250	240
2	9	221	216
2	11	274	261
3	1	262	293
3	3	296	310
3	4	167	140
3	7	400	415
4	0	805	791
4	1	295	302
4	2	180	191
4	3	767	714
4	4	323	329
4	5	466	464
4	6	209	159
4	7	357	325
4	8	335	345
4	11	262	261
5	0	295	276
5	1	603	585
5	2	218	236
5	3	301	262
5	4	605	605
5	5	188	153
5	7	345	375
5	8	242	240
5	9	190	205
5	10	236	257
6	0	385	386
6	2	239	232
6	3	459	501
6	5	351	395
7	0	236	225
7	3	193	142
7	4	398	396
7	6	190	186
8	3	336	322
8	5	260	293
8	8	197	198
9	1	286	305
9	2	154	234
9	4	360	331
9	7	220	249
10	0	327	237
10	3	247	237
H = 8**			
0	0	1116	1124
0	1	1307	1282
0	2	297	293
0	3	798	815
0	4	324	331
0	5	624	621
0	6	246	251
0	7	603	604
0	8	479	475
0	9	566	568
0	11	418	422
1	1	450	440
1	2	688	695
1	3	148	62
1	4	873	879
1	6	808	815
1	7	449	451
1	8	638	651
1	9	278	252
1	10	501	494
1	12	353	363
2	1	1130	1137
2	3	773	776
2	4	196	203
2	5	623	634
2	6	268	268
2	7	644	650
2	8	224	240
2	9	531	523
2	11	332	328
3	0	1256	1240
3	1	430	418
3	2	986	980
3	3	267	245
3	4	620	604
3	5	181	138
3	6	575	559
3	8	535	534
3	10	321	343
4	0	893	893
4	1	990	973
4	2	229	254
4	3	505	499
4	4	309	286
4	5	463	458
4	6	217	188
4	7	722	695
4	8	428	443
4	9	540	567
4	11	296	273
5	0	818	815
5	1	721	728
5	2	602	594
5	3	422	411

Table 21 (continued)

K	L	FOBS	FCAL
**H =		8****	
5	4	435	445
5	5	214	223
5	6	650	639
5	7	648	632
5	8	653	637
5	9	306	360
5	10	327	351
6	0	667	683
6	1	571	581
6	2	207	187
6	3	583	569
6	4	216	215
6	5	574	536
6	6	201	205
6	7	460	466
6	8	383	345
6	9	348	350
7	0	444	477
7	2	519	519
7	3	271	245
7	4	556	534
7	5	241	259
7	6	418	416
7	8	288	327
8	0	628	665
8	1	261	268
8	3	575	575
8	4	697	714
8	5	537	519
8	7	253	247
8	8	259	257
9	0	460	471
9	1	251	231
9	2	520	512
9	3	567	568
9	4	455	452
9	5	316	345
9	6	239	221
10	1	211	170
10	2	177	174
10	3	369	371
10	4	296	324
**H =		9****	
1	0	812	809
1	1	572	574
1	3	332	294
1	4	685	673
1	7	187	172
1	8	442	430
1	9	222	243
2	1	338	336
2	3	696	718
2	5	375	374
2	7	535	549
2	9	256	271
2	11	251	282
3	0	270	250
3	4	251	248
4	0	326	292
4	2	361	330
4	4	710	705
4	7	227	238
4	8	309	300
4	10	178	143
5	0	377	384
5	1	624	647
5	3	507	486
5	4	302	306
5	5	523	542
5	6	224	140
5	8	305	290
6	0	369	359
6	1	201	210
6	2	215	204
6	4	630	640
7	1	390	390
7	3	411	410
7	5	201	153
8	2	211	207
8	4	326	349
8	6	179	142
9	0	214	203
9	3	300	333
9	5	342	339
10	2	235	223
**H =		10****	
0	0	1334	1351
0	1	965	965
0	2	508	547
0	3	295	265
0	5	288	282
0	6	550	552
0	7	589	570
0	8	801	793
0	9	345	348
0	10	189	213
1	0	479	472
1	1	776	795
1	2	391	403
1	4	391	393
1	5	270	251
1	6	528	531
1	7	848	846
1	8	465	449
1	9	536	536
1	10	255	238
2	0	1338	1329
2	1	486	470
2	2	560	560
2	3	526	516
2	5	472	460
2	6	457	476
2	7	375	333
2	8	695	730
2	9	265	285
2	10	182	212
2	11	257	273
3	0	610	605
3	1	859	840
3	2	661	641
3	3	323	316
3	4	525	541
3	5	310	285
3	6	262	297
3	7	545	524
3	9	310	330
3	10	203	205
4	0	485	517
4	1	577	575
4	2	598	557
4	3	305	270
4	4	528	525
4	5	276	270
4	6	319	328
4	7	477	449
4	8	202	213
4	9	347	354
4	10	200	244
5	0	640	625
5	2	221	247
5	3	729	717
5	5	592	597
5	6	487	463
5	8	555	603
5	9	195	177
6	1	528	532
6	2	350	361
6	3	293	229
6	4	707	716
6	5	249	241
6	6	283	279
6	7	262	368
6	9	237	239
7	0	319	315
7	1	365	347
7	2	369	357
7	3	379	375
7	4	347	353
7	5	282	298
7	6	194	219
7	7	254	225
8	0	402	375
8	2	202	228
8	3	532	520
8	5	422	421
8	6	267	291
9	1	476	459
9	2	325	327
9	4	456	460
**H =		11****	
1	0	362	354
1	1	418	462
1	3	480	502
1	4	271	260
1	5	290	341
1	7	403	379
1	10	179	166
2	0	669	658
2	1	358	379
2	3	546	559
2	4	546	558
2	5	357	387
2	7	318	317
2	8	427	418
3	0	497	522
3	3	221	165
3	4	566	575
3	8	239	245
4	3	415	407
4	5	239	238
4	7	216	126
5	0	375	348
6	0	272	312
6	3	241	183
7	1	233	218
7	4	230	215
8	3	199	207
8	5	170	167
9	0	213	205
**H =		12****	
0	0	1012	1017
0	1	503	526
0	2	750	736
0	4	402	412
0	6	421	429
0	7	213	225
0	8	323	351
0	10	189	204
1	0	576	537
1	1	614	623
1	2	205	194
1	3	556	554
1	5	569	525
1	6	220	233
1	7	450	455
1	8	335	336
1	9	291	303
2	0	595	564
2	1	600	592
2	2	526	539
2	3	197	208
2	4	549	524
2	6	452	467
2	7	499	498
2	8	407	411
2	9	273	273
2	10	346	363
3	0	524	503
3	3	649	663
3	4	239	176
3	5	633	651
3	6	298	298
3	7	315	313
3	8	467	445
3	9	325	313
4	2	453	454
4	4	798	798
4	6	438	409
4	9	175	128
5	1	370	385
5	2	288	242
5	3	654	644
5	4	490	470
5	5	524	506
6	0	465	477
6	2	494	505
6	3	381	391
6	4	463	449
6	5	239	263
6	6	270	255
7	1	441	458
7	3	307	297
7	4	221	153
7	5	220	270
8	0	341	357
8	1	210	220
8	2	277	266
8	4	166	205
**H =		13****	
1	1	300	346
1	3	329	297
1	5	271	254
2	0	475	461
2	4	357	408
4	0	393	404
4	1	355	306
5	0	231	203
5	1	249	260
5	7	231	216
6	0	221	224
6	1	295	284
6	3	253	249
7	0	656	665
7	4	342	357
8	1	198	229
**H =		14****	
0	0	637	610
0	1	501	499
0	3	628	646
0	4	282	298
0	5	458	484
0	8	218	222
1	2	419	416
1	4	691	688
1	6	372	419
2	0	225	259
2	1	371	360
2	3	608	574
2	5	495	502
2	7	271	272
3	0	457	464
3	2	562	571
3	3	362	353
3	4	579	575
3	6	311	305
3	7	218	237
4	0	205	149
4	1	359	356
4	3	542	528
4	4	272	227
4	5	474	432
4	7	236	203
5	2	346	328
5	4	614	592
5	6	383	349
6	1	220	229
6	3	511	500
6	5	435	427
7	0	476	469
7	2	321	320
**H =		15****	
1	3	225	126
2	1	220	199
3	0	353	361
3	4	247	302
4	1	303	284
4	3	309	279
5	0	223	234
5	1	243	237
5	4	216	185
6	0	230	273
**H =		16****	
0	0	298	293
0	1	327	328
0	2	350	337
0	4	846	814
1	0	487	459
1	3	607	601
1	5	491	498
2	0	411	395
2	1	395	404
2	2	345	363
2	4	284	285
3	0	227	174
3	1	425	431
3	2	210	186
3	3	202	220
3	4	205	178
3	5	255	199
4	0	403	400
4	2	305	305
4	3	285	264
4	4	215	206
4	5	236	246
5	1	245	245
5	3	315	267
**H =		17****	
2	0	280	272
3	0	216	203
3	3	199	182
4	0	273	214
**H =		18****	
0	0	527	544
0	2	357	405
0	3	337	323
1	1	241	249
1	2	201	199
1	3	225	212
2	0	273	271
2	1	221	206

TABLE 22: ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Mo	0.08815(5)	0.25886(7)	0.25	2.46*
S1	0.0077(1)	0.1371(1)	0.3802(1)	3.28*
S2	0.0632(1)	0.4286(1)	0.3808(1)	3.48*
S3	0.1939(1)	0.2047(1)	0.3808(1)	3.36*
C1	-0.0757(4)	0.0681(5)	0.3096(5)	3.19*
C2	-0.1390(5)	0.0016(7)	0.3648(7)	4.51*
C3	-0.1989(4)	-0.0638(7)	0.3087(7)	4.94*
C4	0.0787(4)	0.5741(5)	0.3091(5)	3.32*
C5	0.0872(5)	0.6936(6)	0.3659(6)	4.55*
C6	0.0959(5)	0.8080(6)	0.3088(7)	6.00*
C7	0.2557(4)	0.0951(6)	0.3091(5)	3.26*
C8	0.3073(4)	0.0067(7)	0.3677(7)	4.30*
C9	0.3565(4)	-0.0801(7)	0.3096(7)	5.30*
H1	-0.1389	0.0016	0.4488	5.2
H2	-0.2438	-0.1121	0.3518	6.0
H3	0.0873	0.6937	0.4499	5.2
H4	0.1023	0.8921	0.3514	6.0
H5	0.3074	0.0066	0.4516	5.2
H6	0.3925	-0.1429	0.3523	6.0

*These values are equivalent isotropic temperature factors[81] corresponding to the anisotropic thermal parameters shown in Table 23.

TABLE 23: ANISOTROPIC TEMPERATURE FACTORS ($\mathring{A}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.0389(4)	0.0259(3)	0.0287(3)	-0.0003(4)	0.0	0.0
S1	0.0489(10)	0.0400(8)	0.0356(8)	-0.0053(8)	-0.0006(9)	0.0033(8)
S2	0.0547(11)	0.0364(8)	0.0409(9)	0.0026(8)	0.0030(9)	-0.0070(8)
S3	0.0455(10)	0.0461(9)	0.0358(8)	0.0015(8)	-0.0049(8)	-0.0027(7)
C1	0.039(4)	0.034(3)	0.048(4)	0.002(3)	0.000(3)	-0.001(3)
C2	0.051(5)	0.064(5)	0.056(5)	-0.006(4)	0.014(4)	0.016(4)
C3	0.039(4)	0.074(5)	0.075(6)	-0.019(4)	0.012(4)	0.008(4)
C4	0.034(4)	0.033(3)	0.059(4)	0.004(3)	-0.002(3)	-0.007(3)
C5	0.057(5)	0.040(3)	0.075(5)	0.015(4)	0.004(5)	-0.013(4)
C6	0.079(6)	0.037(4)	0.111(7)	0.011(4)	0.005(5)	-0.010(4)
C7	0.034(4)	0.044(4)	0.046(4)	-0.000(3)	-0.002(3)	-0.004(3)
C8	0.048(5)	0.061(4)	0.054(5)	0.005(4)	-0.001(4)	0.004(4)
C9	0.045(5)	0.068(5)	0.088(7)	0.011(4)	-0.009(4)	0.014(4)

TABLE 24: INTRAMOLECULAR CONTACTS (Å)

ATOMS	DISTANCE (Å)	ATOMS	DISTANCE (Å)
Mo-S1	2.370(2)	Mo-S2	2.360(2)
Mo-S3	2.371(2)	S1-S1'	3.100(3)
S2-S2'[a]	3.115(3)	S3-S3'	3.114(3)
S1-S2	3.099(2)	S1-S3	3.074(2)
S2-S3	3.101(2)	S1-C1	1.731(6)
S2-C4	1.728(6)	S3-C7	1.721(6)
C1-C1'	1.419(11)	C1-C2	1.388(8)
C2-C3	1.349(10)	C3-C3'	1.394(16)
C4-C4'	1.408(12)	C4-C5	1.398(8)
C5-C6	1.355(8)	C6-C6'	1.400(16)
C7-C7'	1.408(12)	C7-C8	1.410(8)
C8-C9	1.373(10)	C9-C9'	1.418(16)

[a] Primed atoms are related by a mirror at z = 1/4.

TABLE 25: INTRAMOLECULAR ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Mo-S1'[a]	81.70(8)	S2-Mo-S2'	82.57(8)
S3-Mo-S3'	82.09(8)	S1-Mo-S2	81.85(5)
S1-Mo-S3	80.85(6)	S2-Mo-S3	81.89(6)
S1-Mo-S2'	136.17(7)	S1-Mo-S3'	134.43(6)
S2-Mo-S3'	136.51(7)	Mo-S1-C1	108.5(2)
Mo-S2-C4	106.1(2)	Mo-S3-C7	103.9(2)
S1-C1-C1'	119.0(2)	S2-C4-C4'	119.6(2)
S3-C7-C7'	119.7(2)	C2-C1-C1'	118.2(4)
C1-C2-C3	122.1(8)	C2-C3-C3'	119.7(5)
C5-C4-C4'	118.9(4)	C4-C5-C6	120.9(7)
C5-C6-C6'	120.1(4)	C8-C7-C7'	119.7(4)
C7-C8-C9	120.0(7)	C8-C9-C9'	120.3(5)
S3-S1-S2	60.30(5)	S1-S3-S2	60.24(5)
S1-S2-S3	59.46(5)		

[a] Primed atoms are related by a mirror at z = 1/4.

TABLE 26: INTERMOLECULAR CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H4	x, y-1, z	2.941
S1	H3	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.065
S2	H5	1/2-x, 1/2+y, $\bar{z}$+1	2.992
S3	H1	$\bar{x}$, $\bar{y}$, $\bar{z}$+1	3.051
S1	C6	x, y-1, z	3.736(7)
S1	C5	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.800(7)
S2	C8	1/2-x, 1/2+y, $\bar{z}$+1	3.734(8)
S2	C9	1/2+x-1, 1/2-y, z	3.763(7)
S3	C2	$\bar{x}$, $\bar{y}$, $\bar{z}$+1	3.791(7)
S2	S2	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.782(3)
C3	C4	1/2+x-1, 1/2-y, z	3.581(9)
C3	C9	1/2+x-1, 1/2-y-1, z	3.733(10)
C3	C5	1/2+x-1, 1/2-y, z	3.749(10)
C4	C9	1/2+x-1, 1/2-y, z	3.577(9)
C4	C3	1/2+x, 1/2-y, z	3.581(9)
C4	H6	1/2+x-1, 1/2-y, z	3.120
C5	H6	1/2+x-1, 1/2-y, z	3.180
C4	H2	1/2+x, 1/2-y, z	2.927
C5	H2	1/2+x, 1/2-y, z	2.848

TABLE 27: LEAST SQUARES PLANE CALCULATIONS[a]

(A) ATOMS DEFINING PLANE: S1, Mo, S1'

EQUATION OF PLANE: $-0.6913X + 0.7225Y - 0.9227 = 0.0$

(B) ATOMS DEFINING PLANE: S2, Mo, S2'

EQUATION OF PLANE: $-0.9740X - 0.2266Y + 1.9797 = 0.0$

(C) ATOMS DEFINING PLANE: S3, Mo, S3'

EQUATION OF PLANE: $-0.3080X - 0.9514Y + 2.9444 = 0.0$

(D) ATOMS DEFINING PLANE: S1, S2, S3

EQUATION OF PLANE: $-0.0016X - 0.0019Y + 1.0Z - 4.5264 = 0.0$

DISTANCE OF Mo FROM PLANE (Å): -1.556

(E) ATOMS DEFINING PLANE: S1', S2', S3'

EQUATION OF PLANE: $0.0016X - 0.0019Y + 1.0Z - 1.4298 = 0.0$

DISTANCE OF Mo FROM PLANE (Å): 1.556

(F) ATOMS DEFINING PLANE: S1, S1', C1, C1', C2, C2', C3, C3'

EQUATION OF PLANE: $0.5094X - 0.8605Y + 1.1429 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S1	0.005(2)	S1'	0.005(2)
C1	-0.074(6)	C1'	-0.074(6)
C2	-0.011(7)	C2'	-0.011(7)
C3	0.071(8)	C3'	0.071(8)
Mo	-0.4017(7)		

TABLE 26 (Continued)

(G) ATOMS DEFINING PLANE: S2, S2', C4, C4', C5, C5', C6, C6'

EQUATION OF PLANE: $-0.9899X + 0.1420Y + 0.3898 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S2	0.002(2)	S2'	0.002(2)
C4	-0.035(6)	C4'	-0.035(6)
C5	0.001(7)	C5'	0.001(7)
C6	0.028(8)	C6'	0.028(8)
Mo	-0.6412(7)		

(H) ATOMS DEFINING PLANE: S3, S3', C7, C7', C8, C8', C9, C9'

EQUATION OF PLANE: $0.7424X + 0.6700Y - 3.7136 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S3	0.000(2)	S3'	0.000(2)
C7	-0.008(6)	C7'	-0.008(6)
C8	0.006(7)	C8'	0.006(7)
C9	0.001(7)	C9'	0.001(7)
Mo	-0.8942(7)		

[a] X, Y, and Z are in Å and refer to the orthogonal coordinates along *a*, *b*, and *c**.

TABLE 28: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
S1,Mo,S1'	S2,Mo,S2'	120.7°
S1,Mo,S1'	S3,Mo,S3'	118.2°
S2,Mo,S2'	S3,Mo,S3'	121.1°
S1,Mo,S1'	S1,S1',C1,C1',C2,C2',C3,C3'	13.1°
S2,Mo,S2'	S2,S2',C4,C4',C5,C5',C6,C6'	21.1°
S3,Mo,S3'	S3,S3',C7,C7',C8,C8',C9,C9'	30.0°

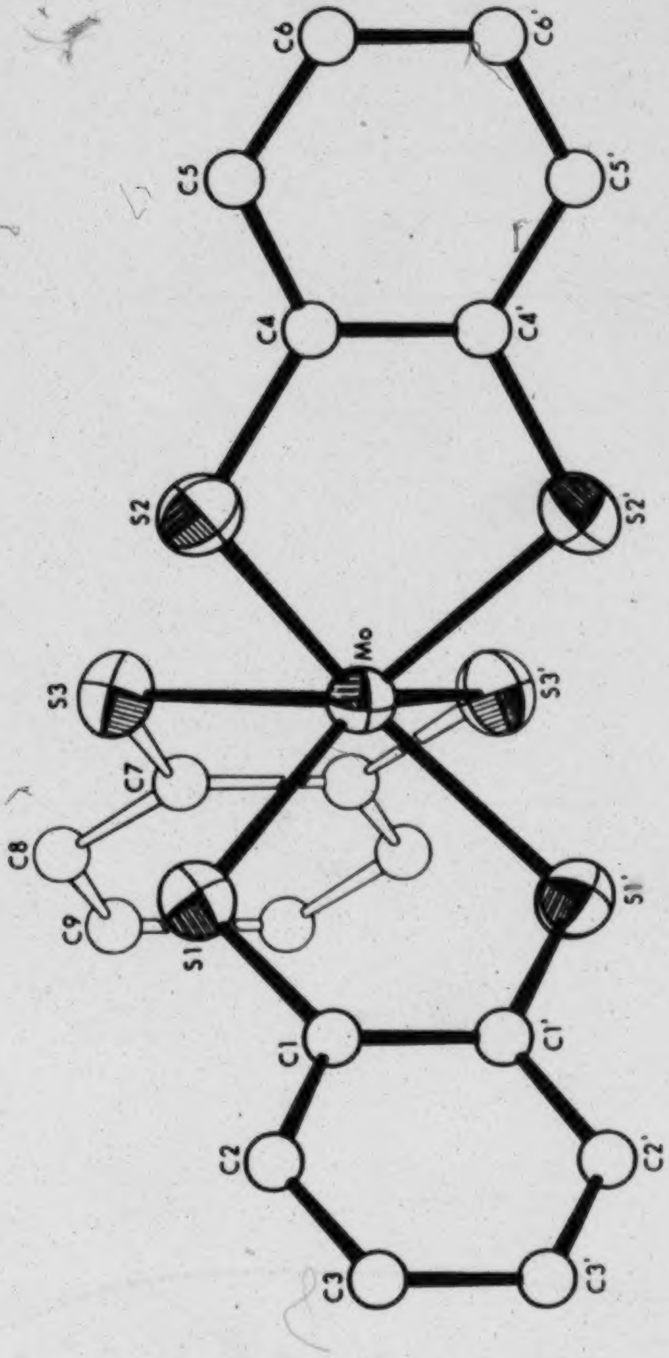

C6
C6'
C5
C5'
C4
C4'
S2
S2'
Mo
S3
S3'
C7
C8
C9
S1
S1'
C1
C1'
C2
C2'
C3
C3'

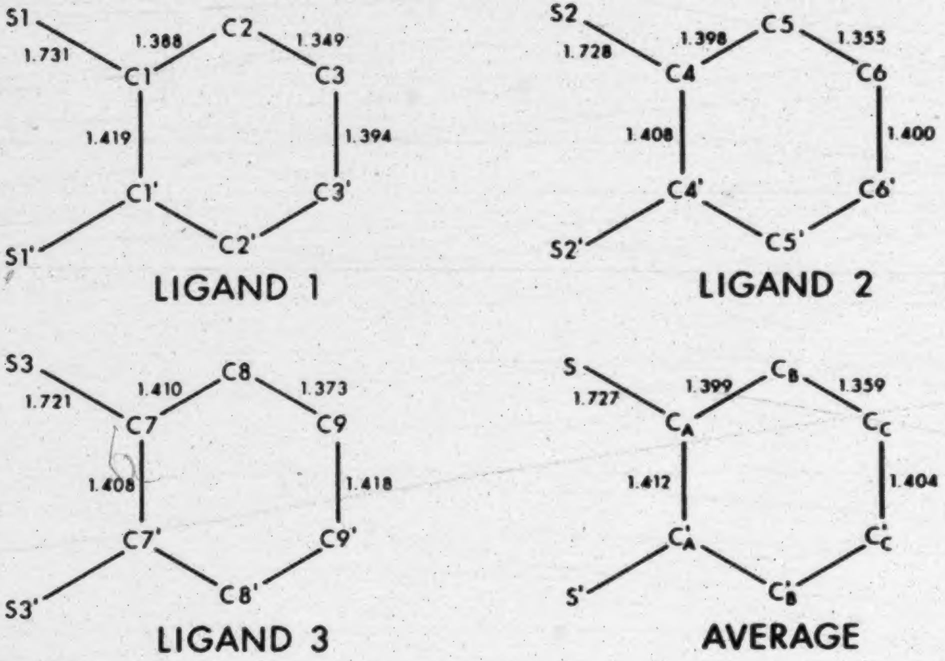
Fig. 9: A PERSPECTIVE VIEW OF $Mo(S_2C_6H_4)_3$.

DESCRIPTION OF STRUCTURE

A 3-dimensional view of Mo(bdt)$_3$ is shown in Fig. 9. The sulfur atoms surround the molybdenum in an almost perfect trigonal prismatic coordination with the dithiolene ligands radiating from the molybdenum atom in a "paddle-wheel" arrangement. The molecule deviates from approximate D_{3h} symmetry due to the bending of the $(S_2C_6H_4)$ planes from the MoS_2 planes by an average of 21.4°. In addition C_{3h} symmetry is not achieved due to the three differing $(S_2C_6H_4)/MoS_2$ dihedral angles (Fig. 12). The molybdenum atom is located on the crystallographic mirror at $z = 1/4$, with the two triangular faces of the prism being related by the mirror.

Again, as was the case for the three previous trigonal prismatic structures, $Re(S_2C_2Ph_2)_3$,[129] $Mo(S_2C_2H_2)_3$[130] and $V(S_2C_2Ph_2)_3$,[132] the intra- and interligand sulfur-sulfur distances are approximately equal (3.110 Å and 3.091 Å respectively in the present study). These agree favourably with those observed in other prisms and are especially close to those in $Mo(S_2C_2H_2)_3$ (Table 48). It is interesting that the relative magnitudes of these intra- and interligand S-S distances are reversed to those in the other three dithiolene trigonal prisms, with the intraligand S-S distances being greater in the present study. This can be attributed to the constraint of the fixed ligand bite holding the intraligand sulfurs apart. That the ligand bite should be greater in the benzene dithiols than in the ethylene dithiols is apparent since the C-C distances in the former are longer, thereby ensuring a larger bite. This was also observed in the trigonal prismatic molecule[152] $Mo[Se_2C_2(CF_3)_2]_3$, which also has intraligand Se-Se distances which exceed the interligand values [3.317(5) Å and 3.222(3) Å respectively].

The mean Mo-S distance (2.367 Å), although similar to the metal-sulfur distance in other trigonal prisms, is significantly longer than their average of approximately 2.33 Å. In fact they are more closely matched by the metal-sulfur distances in the non-trigonal prismatic species $V(mnt)_3^{2-}$ [140] and $Mo(mnt)_3^{2-}$ [141] (Table 48). This difference is again probably due to the difference in ligands, all previous examples being substituted ethylene dithiol ligands. For this reason a rigid comparison of intramolecular distances and angles will prove more worthwhile within the series of compounds which are the topic of part of this thesis, i.e., $Mo(bdt)_3$, $[Ph_4As][Nb(bdt)_3]$, and $[(CH_3)_4N]_2[Zr(bdt)_3]$. In addition the molybdenum-


S1
1.731
C1
1.388
C2
1.349
C3
1.419
1.394
C1'
C3'
C2'
S1'
S2
1.728
C4
1.398
C5
1.355
C6
1.408
1.400
C4'
C6'
C5'
S2'
S3
1.721
C7
1.410
C8
1.373
C9
1.408
1.418
C7'
C9'
C8'
S3'
S
1.727
C_A
1.399
C_B
1.359
C_C
1.412
1.404
C'_A
C'_C
C'_B
S'

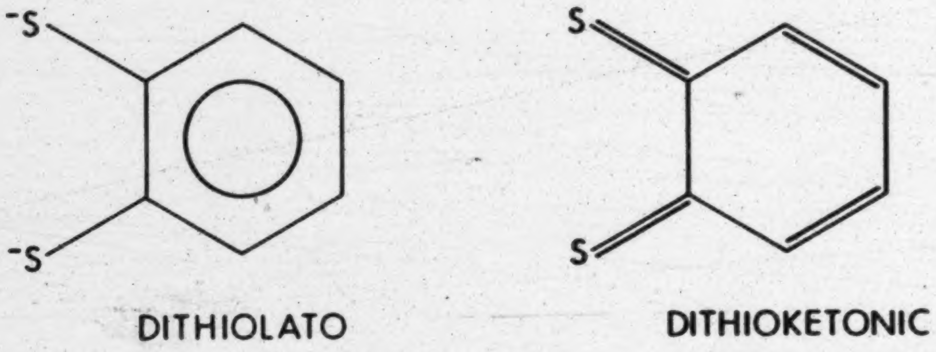
LIGAND 1

LIGAND 2

LIGAND 3

AVERAGE

Fig. 10: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.



DITHIOLATO

DITHIOKETONIC

Fig. 11: DITHIOLATO AND DITHIOKETONIC LIMITING FORMULATIONS FOR THE "bdt" LIGAND.

sulfur distances are again shorter than those observed in the 1,1-dithiolato complexes, $Fe[S_2CN(n\text{-}C_4H_9)_2]_3$,[153] $Ru[S_2CN(C_2H_5)_2]_3$,[154] $Cr[S_2P(CH_3)_2]_3$,[155] and $V[S_2P(OC_2H_5)_2]_3$,[156] although the molybdenum covalent radius is greater than any of these metal radii.[133] Thus a difference in the metal-sulfur bonding between the 1,1-dithiolato and 1,2-dithiolene complexes is obvious with the latter having a greater amount of M-S bonding. This is in agreement with the proposed metal-sulfur multiple bonding in the *tris*(1,2-dithiolenes).[157]

The sulfur-carbon distances (mean 1.727 Å) are similar to those in the other trigonal prisms and are once again consistent with a great deal of S=C double bond character, as witnessed by their similarity with the double bonded S=C distance of 1.72 Å in thiourea[134] $[SC(NH_2)_2]$ and its derivatives.[135] The mean carbon-carbon distance (1.393 Å) is similar to that observed in benzene[158] (1.398 Å) and in several di-substituted benzene compounds.[159] However in the benzene dithiol ligands in this structure there is a significant range of C-C distances (Fig. 10). In addition, these distances are consistent with a tendency towards the dithioketonic limit (Fig. 11). However caution must be used since the dithioketonic limit will not be attained due to other resonance structures, so only a trend towards this limit is noted. Also due to increasing thermal motion of the carbon atoms as the distance from the central atom (Mo) increases, the bonds will appear shorter due to libration of the rings. Thus the shortening of $C_B - C_C$ (Fig. 10) could be partly attributed to thermal motion. However thermal motion of this type cannot cause bond lengthening, so the longer $C_A - C_A'$ bond remains as good evidence of the tendency of the ligand towards its oxidized formulation. At this point it is convenient to note that the thermal parameters in this and similar structures all show an anomalous feature. In molecules of this type it would appear reasonable to expect that the general trend of thermal amplitudes increases steadily as one progresses outward from the centre of gravity of the molecule. This assumes that the thermal motion is dominated by rigid body motion. However the sulfur atoms have larger thermal parameters than their attached carbon atoms. This observation, which appears to be very general for sulfur donor ligands, suggests either the unsuitability of the scattering factors used, or large vibration of the core of the molecule. This feature precludes any attempt at correction of these bond lengths for thermal motion and hence severely restricts the discussion

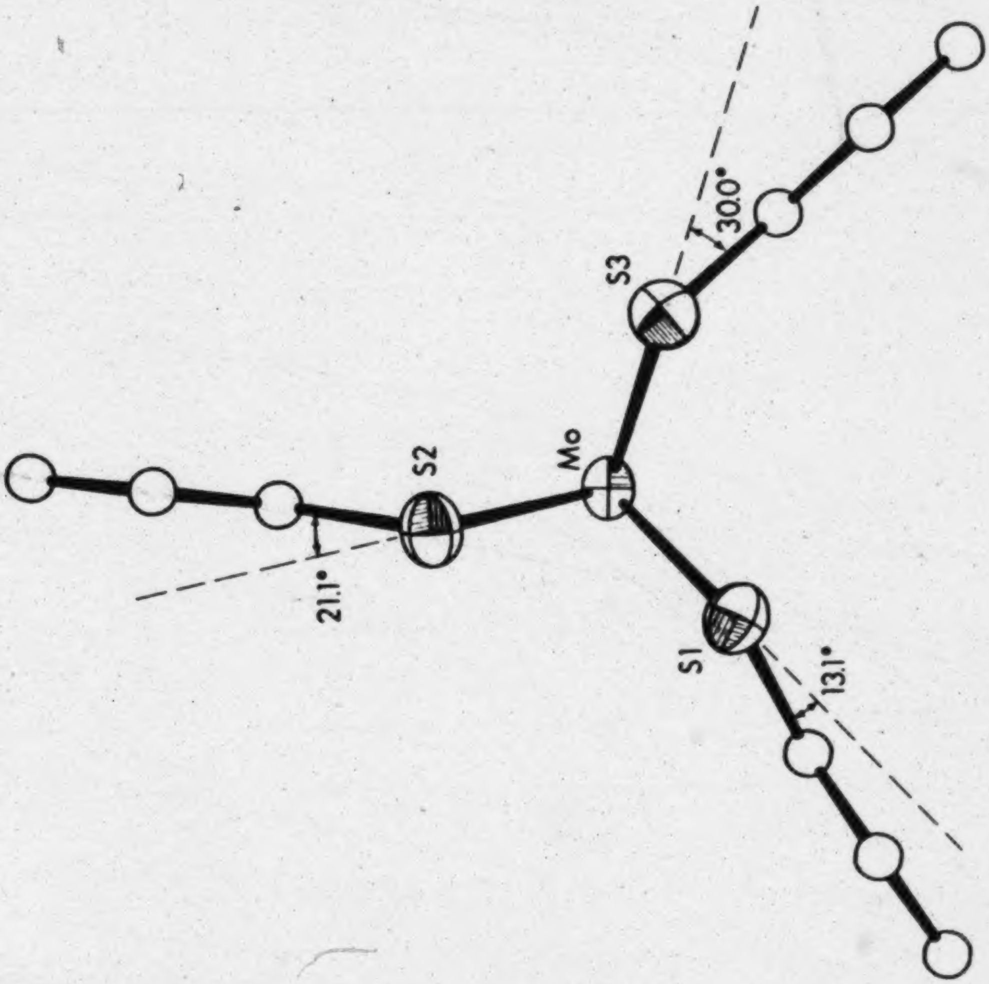

30.0°
S3
S2
Mo
21.1°
S1
13.1°

Fig. 12: VIEW OF $Mo(S_2C_6H_4)_3$ DOWN THE CRYSTALLOGRAPHIC *c* AXIS.

of the ligand geometry with respect to the pattern of carbon-carbon bond lengths. A more complete view of the ligand in its reduced and oxidized formulation is presented in Chapter IX, based on molecular orbital calculations performed by Birss and Das Gupta.[160]

The mean S-M-S angle involving *trans* sulfur atoms is 136 ± 1° in the known trigonal prismatic structures,[129,130,132] and assuming the constraint of ligand bite, has been calculated[161] as approximately 173° in octahedral coordination. The mean value of 135.70° observed in $Mo(bdt)_3$ is clearly consistent with trigonal prismatic coordination. The intra- and interligand S-Mo-S angles (82.12° and 81.53°) are similar, as expected, and again agree with those found in other trigonal prismatic structures.[129,130,132]

As mentioned, the molecule deviates from D_{3h} symmetry due to the bend of the ligand planes from the respective S-Mo-S planes, as shown in Fig. 12, in which the molecule is viewed directly down the crystallographic *c* axis and approximate molecular three-fold axis. Similar bending of the ligand planes was observed in $Mo(S_2C_2H_2)_3$[130] and also in $Mo(Se_2C_2(CF_3)_2)_3$,[152] where the ligand planes deviate from the MoS_2 and $MoSe_2$ planes by 18° and 18.6° respectively. Although these deviations are uniform in these previous two examples, the molecules both having 3/m symmetry, they are irregular for Mo(bdt)$_3$ with the ligand/MoS$_2$ dihedral angles being 13.1°, 21.1°, and 30.0° (mean 21.4°). Schrauzer[130] has attributed this as being due to intramolecular effects, saying that the sulfur may be in a state between sp^2 and sp^3 hybridization, with possible added stabilization from packing forces. However from the structure of Mo(bdt)$_3$ it is obvious that packing forces contribute significantly, as witnessed by the wide range in dihedral angles observed. Table 26 shows that several intermolecular contacts are comparable to the predicted van der Waals contacts[151] (Predicted values: S···C, 3.70 Å; S···S, 3.70 Å; S···H, 3.05 Å; C···C, 3.70 Å; C···H 3.05 Å; H···H, 2.40 Å). Thus packing is very efficient and will probably be important in the bending of the ligand planes. A packing diagram, viewed down the *c* axis is shown in Fig. 13. The efficient packing is obvious from this diagram with the molecules packing in a gear-wheel arrangement.

As shown in Table 28, a further indication of the regularity of the prism is given by the similarity of the angles between the three MoS$_2$ planes, all being close to the expected value of 120°. The two tri-

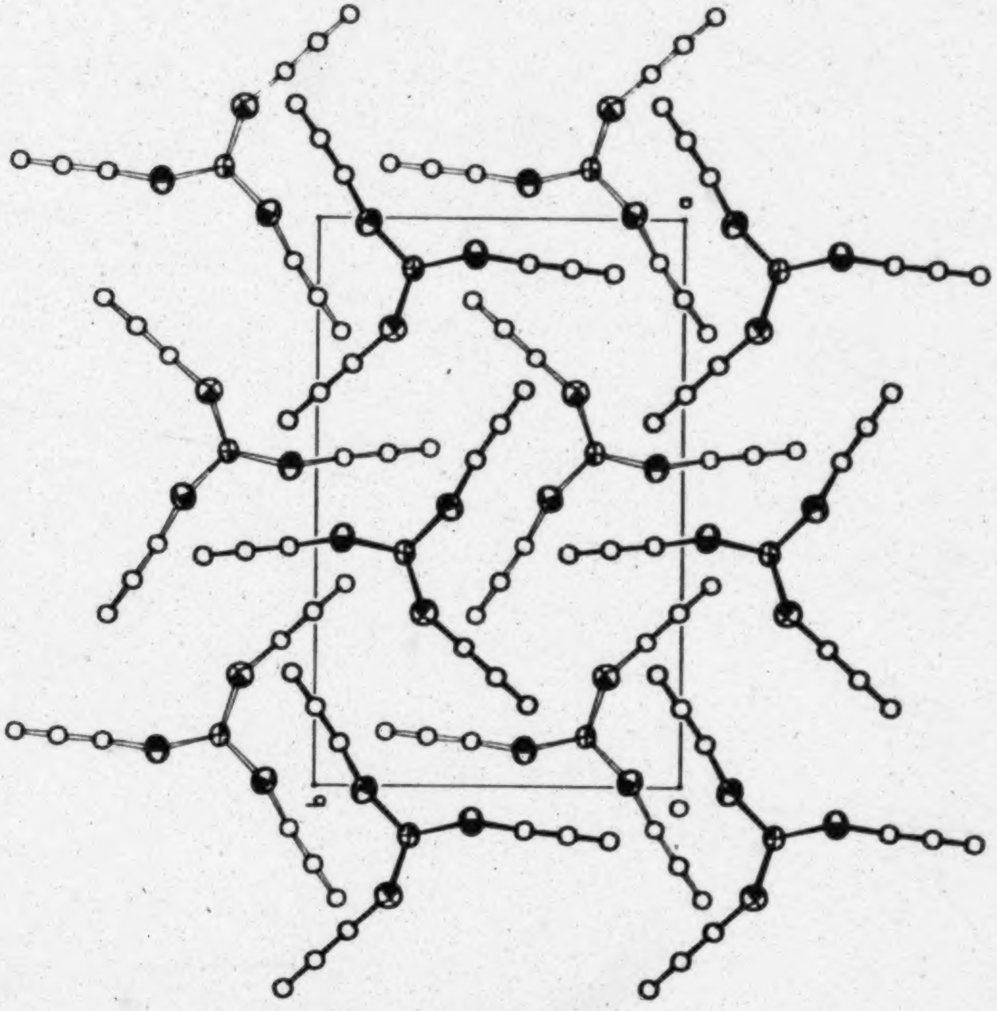


Fig. 13: PACKING DIAGRAM FOR $Mo(S_2C_6H_4)_3$, PROJECTED ON THE *ab* PLANE.

angular faces of the prism are also almost exactly parallel.

The Mo-S-C angles (mean 106.2°) are similar to the values of 109(1)° and 109.9(4)° observed in $Re(S_2C_2Ph_2)_3$ and $V(S_2C_3Ph_2)_3$, however they are significantly smaller, again probably due to differences in the ligands. The S-C-C' angles (mean 119.4°) are in good agreement with the value of 120°. Similarly all C-C-C angles within the benzene rings are close to their expected value of 120°.

CHAPTER VII: THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAPHENYLARSONIUM *TRIS* (BENZENE-1,2-DITHIOLATO) NIOBIUM, ($[(C_6H_5)_4As][Nb(S_2C_6H_4)]$)

EXPERIMENTAL

Dark purple crystals suitable for single crystal X-ray diffraction study, prepared by the reaction of sodium cyclopentadienide with benzene dithiol and subsequent reaction with $Nb[N(CH_3)_2]_5$ and crystallization with tetraphenylarsonium chloride,[143] were kindly supplied by Dr. Takats and Mr. Martin. Preliminary photography indicated 2/m Laué symmetry consistent with a monoclinic space group. Systematic absences, as determined by Weissenberg ($h0\ell$, $h1\ell$; CuK_α X-radiation) and Precession photographs ($0k\ell$, $1k\ell$, $hk0$, $hk1$; MoK_α X-radiation), are $0k0$: $k = 2n + 1$ and $h0\ell$: $h + \ell = 2n + 1$ indicating the non-standard space group $P2_1/n$, which was retained because of the convenient β angle. The cell parameters, obtained at 22°C from a least squares analysis of the setting angles of 12 reflections, which were centred accurately on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation ($\lambda = 1.54051$ Å), are: $a = 22.983(7)$ Å, $b = 12.747(4)$ Å, $c = 13.150(3)$ Å, $\beta = 92.09(2)°$. The observed density, obtained by floatation in aqueous zinc bromide solution, is 1.52(2) g cm^{-3} and is in reasonable agreement with the theoretical value of 1.54 g cm^{-3} calculated assuming four molecules with formula weight 896.94 a.m.u. per unit cell of volume 3867.12 $\mathring{A}^3$.

Intensity data were collected on the Picker automatic diffractometer, using CuK_α X-radiation, filtered using a 0.0005" thick Ni foil, and using a 2° take-off angle. The crystal was aligned in a general orientation but with its b^* axis approximately coincident with the ϕ axis of the instrument. Crystal faces were identified and perpendicular distances between faces of the same form were measured as: $\{1,0,0\}$, 0.206 mm; $\{\bar{2},1,0\}$, 0.206 mm; $\{\bar{2},\bar{1},0\}$, 0.206 mm; $\{\bar{1},0,1\}$, 0.155 mm; $\{1,0,1\}$, 0.175 mm.

In the data collection a coupled $2\theta/\omega$ scan was used with a 2θ scan speed of 1°/min to collect all reflections with $2\theta \leq 115°$. The peak scan was 2° (2 min) for low angle reflections but increased with increasing 2θ due to compensation for $\alpha_1\alpha_2$ separation. Background counts were measured for 20 seconds at the limits of the two theta scan. The scattered X-rays were detected by a scintillation counter used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. Another five standard reflections were collected manually every 10 hours to detect more precisely decomposition and crystal centering errors. No significant decomposition was observed but small fluctuations (± 1%), due to an instability of the goniometer head, were detected. These fluctuations were not regular and corrections were not made.

Of the 5862 unique reflections collected, 3604 were considered as significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. For CuK_α X-radiation, the linear absorption coefficient[86] is 68.42 cm^{-1} which yielded a range of transmission factors of 0.4359 to 0.3128. Standard deviations were estimated using a "p factor" of 0.03 as outlined in Chapter II. Terms used in the Zachariasen[148] extinction correction were calculated at this stage.

TABLE 29: MAJOR PATTERSON PEAKS AND THEIR ASSIGNMENT

OBSERVED VECTOR	RELATIVE INTENSITY	ASSIGNMENT	CALCULATED POSITION[a]
0.500, 0.063, 0.500	250	$1/2, 1/2-2y_1, 1/2$	0.500, 0.064, 0.500
0.339, 0.500, 0.106	226	$1/2-2x_1, 1/2, 1/2-2z_1$	0.340, 0.500, 0.114
0.209, 0.377, 0.532	159	$-(x_1+x_2), (y_1+y_2), -(z_1+z_2)$	0.208, 0.374, 0.544
0.287, 0.440, 0.958	148	$1/2+(x_1+x_2), 1/2-(y_1-y_2), 1/2+(z_1+z_2)$	0.292, 0.438, 0.956
0.130, 0.126, 0.578	146	$1/2-(x_1-x_2), 1/2-(y_1+y_2), 1/2-(z_1-z_2)$	0.132, 0.126, 0.570
0.500, 0.188, 0.500	140	$1/2, 1/2-2y_2, 1/2$	0.500, 0.188, 0.500
0.165, 0.424, 0.395	113	$2x_1, 2y_1, 2z_1$	0.160, 0.436, 0.386
0.078, 0.500, 0.958	103	$1/2-2x_2, 1/2, 1/2-2z_2$	0.076, 0.500, 0.974
0.418, 0.314, 0.532	63	$2x_2, 2y_2, 2z_2$	0.424, 0.312, 0.526

[a] Calculated on the basis of the consistent solution:

$x_1 = 0.580$, $y_1 = 0.218$, $z_1 = 0.193$; $x_2 = 0.212$, $y_2 = 0.156$, $z_2 = 0.263$.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened[146] Patterson was calculated between the limits $0 \le u \le 0.5$, $0 \le v \le 0.5$, $0 \le w \le 1.0$. The general positions for space groups $P2_1/n$ are: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $1/2 + x, 1/2 - y, 1/2 + z$; and $1/2 - x, 1/2 + y, 1/2 - z$. For one niobium [coordinates (x_1, y_1, z_1)] and one arsenic atom [coordinates (x_2, y_2, z_2)] per general position, the major peaks in the map can be assigned as shown in Table 29.

A brief outline of the refinement is shown in Table 30.

TABLE 30: REFINEMENT OUTLINE

	MODEL	R_1	R_2
(1)	Nb and As positions, B's fixed	0.421	0.507
(2)	Nb, As, and S positions, isotropic B's	0.270	0.359
(3)	Nb, As, S with isotropic B's, benzene rings as rigid bodies	0.076	0.087
(4)	Absorption and Extinction[147]	0.064	0.072
(5)	Nb, S, and As anisotropic	0.056	0.065
(6)	Nb, S, and As anisotropic, ligand carbons individual isotropic, H atoms and benzene rings on arsenic as rigid bodies	0.049	0.051
(7)	Model (6) but with anisotropic dithiolene carbons	0.047	0.048

Structure factors were calculated using the atomic scattering factors for the neutral atoms for niobium, arsenic, sulfur, and carbon as tabulated by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] In addition, anomalous dispersion corrections[76] were applied to the niobium, arsenic and sulfur scattering factors ($^{\Delta}f'_{Nb} = -0.58$, $^{\Delta}f''_{Nb} = 2.68$, $^{\Delta}f'_{As} = -1.17$, $^{\Delta}f''_{As} = 1.17$, $^{\Delta}f'_{S} = 0.31$, $^{\Delta}f''_{S} = 0.58$). Features surrounding the Nb, As and S atoms in the electron density difference map suggested the anisotropic refinement, and the validity was verified by a Hamilton's R Test[79] at the 0.005 significance level.

Initially the benzene rings were refined as rigid bodies constrained to their well known geometry. In model (6) the carbon atoms of the benzene dithiol ligands were refined individually with isotropic temperature factors, and the phenyl groups on the arsenic atoms were refined as rigid bodies. The hydrogen positions were calculated from the geometry and orientation of the benzene rings and were also added as rigid bodies, using a C-H distance of 1.0 Å. The hydrogen rigid bodies were not refined however. The final model was refined with anisotropic temperature factors on the carbon atoms of the dithiolene ligands. This was again justified by a Hamilton's R Test[79] at the 0.005 significance level.

In the final least squares refinement, 284 parameters were varied, and the standard deviation in an observation of unit weight was 1.641. The final value of the refined extinction parameter, C, was 8.74×10^{-7}.

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 31. The final fractional coordinates and isotropic B's of all atoms are shown in Table 32. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 33 shows the anisotropic thermal parameters (U_{ij}'s).[80] Intra-ionic contacts and angles, shown in Tables 34 and 35, were obtained with their standard deviations from ORFFE. Inter-ionic contacts (also obtained from ORFFE) are shown in Table 36. Selected least squares planes are given in Table 37. In Table 38, the dihedral angles between some selected planes are shown.

In Fig. 14 a three-dimensional view of the $Nb(bdt)_3^-$ anion is shown. Fig. 16 shows the anion and the

$(C_6H_5)_4As^+$ cation together, viewed down the crystallographic *b* axis. The numbering scheme is shown in both diagrams. For the carbon atoms in the phenyl groups, the first number designates the ring number and the second number is the sequence of the atom in the ring. The carbon atoms are numbered sequentially and for the phenyl groups in the cation the first atom in the numbering scheme is always bonded to the arsenic atom. The hydrogen atoms are not shown but are numbered from H1 to H32 and are bonded, four on each dithiolene ligand and five on each phenyl group, sequentially from C12 to C76.

In the three dimensional representations the niobium, sulfur and arsenic atoms are shown with 50% probability thermal ellipsoids. The carbon atoms are shown, however, with artificially low isotropic thermal parameters, for clarity.

TABLE 31: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 0**				-24	4	225	284	-18	8	281	254	-13	0	186	178	-4	2	474	465
-24	C	392	416	-22	4	425	428	-16	8	486	518	-12	C	332	347	-3	2	1266	1145
-22	0	258	305	-20	4	1304	1315	-14	8	254	240	-10	0	506	520	-2	2	1583	1514
-20	0	710	740	-14	4	436	441	-12	8	1570	1537	-9	0	698	715	-1	2	940	983
-18	0	825	793	-12	4	361	378	-8	8	3C7	287	-8	0	714	765	0	2	377	37C
-14	C	1586	1593	-10	4	1648	1602	-6	8	1253	1312	-7	C	1381	1406	1	2	600	622
-12	C	601	595	-8	4	460	471	-2	8	1567	1593	-6	C	1944	2032	2	2	2044	2137
-10	C	1771	1779	-6	4	701	712	0	8	1366	1422	-4	0	895	876	3	2	231	256
-8	0	1451	1521	-4	4	798	708	2	8	1166	1158	-2	0	3003	3089	4	2	566	561
-6	0	177	177	-2	4	811	808	4	8	542	510	-1	0	229	254	5	2	263	266
-4	0	1442	1445	0	4	482	494	6	8	298	326	1	C	249	254	6	2	895	942
-2	0	150	190	2	4	504	535	8	8	1257	1296	2	0	3070	3089	7	2	264	287
2	0	136	190	4	4	946	965	10	8	220	229	4	0	891	876	8	2	642	671
4	0	1432	1445	6	4	799	891	12	8	712	709	6	C	1994	2032	1C	2	963	1002
8	0	1475	1521	8	4	978	1046	14	8	273	243	7	0	1366	1406	12	2	769	82C
1C	0	1761	1779	10	4	743	813	18	8	795	760	8	C	728	765	13	2	275	214
12	0	609	595	12	4	388	384	20	8	30C	318	9	0	708	715	14	2	188	132
14	0	1555	1593	14	4	1021	1058	-17	9	769	814	10	C	505	520	16	2	691	678
18	0	798	793	16	4	275	254	-15	9	404	401	12	0	319	347	18	2	561	578
2C	0	729	740	20	4	933	923	-13	9	6C4	595	13	0	222	178	19	2	705	721
22	0	242	305	22	4	573	553	-9	9	1045	1046	14	0	485	487	20	2	422	382
24	0	381	416	-23	5	826	885	-7	9	319	366	15	0	235	244	22	2	493	497
-23	1	242	313	-21	5	246	239	-5	9	399	338	16	0	1176	1199	23	2	206	143
-21	1	997	1016	-19	5	358	388	-3	9	12C4	1213	18	0	305	257	-23	3	408	380
-17	1	1234	1260	-17	5	231	254	-1	9	911	958	19	C	653	627	-21	3	1127	1139
-15	1	618	603	-13	5	705	644	1	9	845	845	22	0	519	570	-19	3	253	265
-13	1	943	991	-11	5	199	169	5	9	1517	1506	24	0	198	120	-18	3	365	318
-11	1	299	289	-9	5	1675	1573	7	9	351	355	-23	1	333	347	-17	3	439	438
-9	1	296	305	-7	5	1103	1042	9	9	289	289	-22	1	223	234	-16	3	575	537
-7	1	621	647	-5	5	571	563	15	9	9C1	885	-21	1	398	390	-15	3	358	373
-5	1	852	842	-3	5	341	351	17	9	236	225	-19	1	1257	1246	-14	3	260	266
-3	1	2846	2603	-1	5	239	225	19	9	210	200	-18	1	203	283	-13	3	398	380
-1	1	875	841	1	5	1375	1455	-12	1C	485	549	-17	1	253	232	-12	3	184	84
1	1	1075	1239	3	5	2539	2662	-10	10	332	326	-16	1	665	687	-11	3	831	787
3	1	2074	2196	5	5	308	320	-8	10	603	608	-15	1	276	268	-9	3	850	826
5	1	3145	3123	7	5	699	740	-6	10	998	1051	-13	1	570	597	-8	3	923	91C
7	1	1645	1682	9	5	353	400	-2	10	712	765	-11	1	1367	1369	-7	3	216	201
11	1	1822	1857	11	5	1034	1072	0	10	675	712	-10	1	1061	1036	-6	3	735	706
17	1	1490	1463	15	5	571	536	2	10	1381	1376	-9	1	395	408	-5	3	256	284
19	1	676	707	17	5	817	807	4	1C	653	660	-8	1	562	549	-4	3	1281	1192
21	1	280	325	19	5	853	851	6	10	835	798	-7	1	220	211	-3	3	285	262
23	1	350	307	21	5	297	284	8	10	823	801	-5	1	856	916	-2	3	7C9	671
25	1	211	199	23	5	501	483	12	10	762	751	-4	1	473	468	-1	3	1214	1196
-24	2	566	591	-20	6	950	999	16	10	495	451	-3	1	334	341	0	3	1569	1518
-22	2	274	319	-18	6	380	367	-15	11	231	212	-2	1	1299	12C9	1	3	2907	2826
-20	2	360	412	-16	6	532	541	-9	11	881	876	-1	1	1375	1221	2	3	2163	2226
-18	2	872	906	-14	6	218	254	-5	11	497	477	0	1	428	445	3	3	268	317
-16	2	655	625	-12	6	1225	1212	-1	11	399	374	1	1	2029	2240	4	3	282	260
-12	2	720	649	-1C	6	1123	1167	1	11	599	542	2	1	653	704	5	3	1000	1061
-10	2	1514	1461	-8	6	509	491	9	11	595	576	3	1	1085	1139	6	3	314	333
-8	2	956	941	-6	6	929	927	11	11	754	811	4	1	174	216	8	3	500	528
-6	2	1294	1249	-4	6	321	312	13	11	264	270	5	1	1885	1918	9	3	1737	1795
-4	2	3766	3379	-2	6	902	943	15	11	483	492	6	1	299	294	10	3	329	312
-2	2	2442	2278	0	6	485	436	-10	12	289	311	7	1	869	909	11	3	958	952
0	2	2486	2421	2	6	848	852	-8	12	28C	304	9	1	1626	1699	12	3	633	625
2	2	278	315	4	6	619	627	-6	12	962	1020	10	1	1062	1104	13	3	695	719
4	2	772	770	6	6	352	348	-2	12	221	157	11	1	479	552	14	3	510	528
6	2	1700	1764	10	6	1005	999	4	12	848	925	12	1	289	285	15	3	404	413
8	2	1439	1492	12	6	851	890	6	12	382	356	13	1	923	941	16	3	264	208
12	2	571	594	14	6	538	539	8	12	1C28	1048	14	1	658	655	17	3	454	462
14	2	1566	1637	18	6	383	368	10	12	254	197	15	1	365	333	19	3	767	768
18	2	242	288	2C	6	570	589	12	12	340	349	16	1	861	885	21	3	302	315
20	2	966	997	22	6	738	719	-9	13	550	603	17	1	243	293	22	3	303	292
24	2	371	375	-21	7	281	327	-5	13	592	633	19	1	1144	1146	-24	4	414	438
-23	3	910	909	-19	7	633	596	-1	13	226	248	21	1	228	193	-23	4	293	268
-21	3	580	554	-17	7	773	791	1	13	203	189	22	1	285	283	-22	4	269	250
-19	3	566	525	-15	7	739	726	3	13	549	591	-24	2	309	307	-21	4	280	257
-15	3	525	528	-13	7	597	604	5	13	638	643	-23	2	233	158	-19	4	312	280
-13	3	453	446	-9	7	1301	1308	7	13	430	438	-21	2	302	312	-18	4	803	825
-11	3	495	503	-7	7	832	833	-6	14	337	368	-20	2	305	307	-16	4	289	27C
-9	3	443	332	-5	7	858	844	-2	14	215	238	-19	2	487	440	-14	4	469	476
-7	3	2384	2298	-3	7	1365	1365	2	14	618	622	-18	2	477	482	-13	4	784	796
-5	3	2812	2643	1	7	2691	2655	***K = 1*****				-16	2	606	587	-12	4	371	385
-3	3	1367	1267	3	7	889	857	-24	C	199	12C	-14	2	355	369	-11	4	207	232
-1	3	815	776	5	7	1235	1210	-22	0	568	57C	-13	2	511	479	-9	4	647	624
1	3	792	853	7	7	660	698	-21	C	225	197	-12	2	545	544	-8	4	1256	1233
3	3	1740	1918	9	7	796	795	-19	C	421	627	-10	2	215	192	-7	4	1243	1206
7	3	762	812	11	7	218	246	-18	0	277	257	-8	2	1773	1653	-6	4	164	120
11	3	1404	1476	15	7	1095	1043	-16	0	1167	1195	-7	2	700	704	-5	4	448	440
15	3	652	754	19	7	414	413	-15	0	241	244	-6	2	540	536	-4	4	885	856
17	3	1288	1305	21	7	307	306	-14	C	480	487	-5	2	1157	1148	-3	4	148	127
21	3	529	505	-20	8	950	1015												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 1*				14	6	458	421	2	9	387	403	-13	0	1290	1294	-15	2	451	466
-2	4	957	945	17	6	331	378	3	9	449	465	-12	0	978	985	-14	2	190	204
-1	4	1372	1341	18	6	426	462	7	9	934	965	-11	0	471	460	-13	2	670	659
0	4	250	224	20	6	825	804	12	9	344	308	-10	0	1501	1470	-12	2	492	553
1	4	1212	1245	22	6	295	303	13	9	719	742	-9	0	533	581	-11	2	1096	1083
2	4	1704	1820	-21	7	578	600	14	9	257	251	-8	0	1617	1622	-10	2	1593	1568
4	4	1503	1570	-19	7	389	384	16	9	465	447	-7	0	502	487	-9	2	337	341
7	4	397	386	-15	7	981	988	17	9	328	353	-6	0	1144	1179	-7	2	925	940
8	4	518	509	-14	7	238	215	-18	10	228	196	-5	0	844	872	-6	2	871	905
9	4	1019	1063	-13	7	493	533	-15	10	318	298	-4	0	1705	1676	-4	2	1961	1797
11	4	190	198	-11	7	556	541	-14	10	567	636	-3	0	1492	1508	-3	2	2767	2514
12	4	986	1011	-10	7	586	575	-11	10	209	233	-2	0	1043	1033	-2	2	1123	1062
13	4	716	719	-9	7	850	836	-8	10	475	463	-1	0	265	282	0	2	444	465
14	4	252	260	-7	7	1510	1485	-6	10	275	287	0	0	2940	2998	1	2	294	341
15	4	204	204	-6	7	196	152	-4	10	712	694	1	0	254	282	2	2	426	466
16	4	625	647	-5	7	985	988	-3	10	385	385	2	0	1026	1033	3	2	1270	1371
17	4	272	264	-4	7	431	449	-2	10	415	397	3	0	1514	1508	4	2	598	665
18	4	310	253	-3	7	232	257	-1	10	469	486	4	0	1676	1676	5	2	863	933
19	4	222	258	-2	7	578	605	0	10	536	537	5	0	878	872	6	2	985	1040
20	4	869	900	-1	7	2165	2142	2	10	1022	1021	6	0	1161	1179	7	2	611	604
22	4	871	863	0	7	228	219	3	10	209	199	7	0	508	487	8	2	2114	2174
-23	5	209	226	1	7	257	276	4	10	361	357	8	0	1599	1622	10	2	557	548
-21	5	686	677	2	7	599	617	5	10	224	213	9	0	538	581	11	2	258	263
-18	5	367	378	3	7	789	791	6	10	593	560	10	0	1487	1470	12	2	454	474
-16	5	424	460	4	7	197	171	10	10	982	962	11	0	457	460	13	2	502	513
-15	5	795	778	5	7	225	251	13	10	370	379	12	0	967	985	14	2	383	405
-12	5	368	362	7	7	951	948	16	10	387	375	13	0	1270	1294	17	2	845	889
-11	5	335	306	8	7	228	238	17	10	326	282	14	0	672	699	20	2	574	579
-10	5	298	328	9	7	950	931	-14	11	231	227	15	0	595	603	21	2	288	277
-9	5	761	723	10	7	222	235	-11	11	769	760	17	0	529	549	-24	3	614	646
-8	5	362	361	11	7	962	982	-8	11	830	896	18	0	316	347	-23	3	314	354
-7	5	642	600	12	7	408	433	-7	11	493	845	20	0	387	409	-21	3	330	365
-6	5	479	470	13	7	325	309	-6	11	539	598	21	0	508	539	-20	3	250	220
-5	5	1168	1077	14	7	246	228	-5	11	220	218	24	0	282	291	-19	3	483	502
-4	5	1361	1271	15	7	241	189	-4	11	427	487	-24	1	309	442	-18	3	318	336
-3	5	157	167	17	7	728	702	-3	11	600	725	-21	1	638	664	-16	3	236	264
-2	5	913	882	20	7	251	178	-1	11	361	403	-18	1	326	332	-14	3	857	874
-1	5	1209	1222	-18	8	892	925	0	11	274	211	-16	1	956	880	-13	3	976	937
0	5	316	295	-16	8	457	418	1	11	317	294	-15	1	589	576	-12	3	270	249
1	5	1543	1546	-14	8	818	809	4	11	230	219	-14	1	520	510	-11	3	715	690
2	5	318	297	-13	8	421	407	5	11	302	364	-13	1	1330	1355	-10	3	1504	1452
3	5	961	993	-12	8	634	616	6	11	237	263	-12	1	692	652	-9	3	1545	1303
5	5	679	652	-11	8	269	286	7	11	992	967	-11	1	708	697	-7	3	880	872
6	5	1201	1276	-10	8	754	738	9	11	944	951	-10	1	484	515	-6	3	208	224
9	5	2060	2030	-9	8	241	254	10	11	402	362	-9	1	1625	1594	-4	3	2231	2045
10	5	897	939	-8	8	412	351	11	11	229	136	-8	1	381	365	-3	3	1167	1040
13	5	304	312	-6	8	299	272	13	11	614	627	-7	1	726	728	-2	3	1970	1862
14	5	822	869	-5	8	698	722	-14	12	203	233	-5	1	248	241	-1	3	536	528
15	5	316	320	-4	8	1452	1430	-11	12	400	413	-4	1	1704	1625	0	3	877	874
17	5	447	450	-3	8	470	460	-8	12	563	584	-3	1	1340	1260	1	3	863	883
19	5	784	690	-2	8	632	616	-6	12	484	511	-2	1	1706	1633	2	3	339	356
21	5	536	562	-1	8	594	611	-3	12	391	398	-1	1	1188	1114	3	3	748	795
22	5	287	239	2	8	1676	1703	0	12	304	420	0	1	2069	2080	4	3	605	649
23	5	427	422	3	8	410	389	1	12	312	295	1	1	255	264	5	3	227	255
-22	6	321	322	4	8	798	800	2	12	373	381	2	1	269	342	6	3	444	458
-20	6	211	198	5	8	630	638	4	12	463	451	3	1	3026	3179	7	3	1318	1375
-18	6	1144	1132	6	8	377	387	6	12	296	252	4	1	1506	1550	8	3	1466	1491
-14	6	343	344	7	8	204	216	10	12	860	803	5	1	711	758	9	3	200	174
-12	6	1070	1071	9	8	206	200	11	12	546	509	6	1	1432	1488	10	3	560	520
-11	6	308	253	10	8	929	975	12	12	272	272	7	1	690	712	11	3	1429	1478
-10	6	867	792	12	8	823	836	-11	13	613	650	8	1	842	885	12	3	1292	1311
-9	6	387	357	13	8	429	437	-9	13	253	292	9	1	543	573	13	3	375	371
-8	6	863	825	14	8	491	489	-8	13	212	265	10	1	1334	1393	14	3	940	950
-7	6	[illegible]	776	15	8	411	405	-6	13	498	526	11	1	1477	1476	17	3	543	571
-5	6	662	649	16	8	657	611	-3	13	557	560	12	1	271	244	19	3	340	289
-4	6	2036	1924	17	8	519	479	-1	13	301	313	13	1	462	498	22	3	249	137
-3	6	357	318	18	8	355	298	1	13	315	359	14	1	946	961	23	3	351	342
-2	6	763	649	20	8	521	506	3	13	625	624	16	1	729	763	24	3	328	372
-1	6	486	484	-19	9	477	521	7	13	275	281	17	1	477	467	-23	4	277	309
0	6	497	544	-18	9	265	234	8	13	354	329	18	1	424	468	-22	4	232	245
1	6	483	499	-17	9	327	339	9	13	456	438	19	1	321	360	-21	4	539	535
2	6	470	476	-15	9	220	291	-6	14	362	374	20	1	395	377	-20	4	524	534
3	6	427	415	-14	9	434	412	0	14	694	680	21	1	592	581	-18	4	220	202
4	6	418	403	-13	9	218	326	***K = 2****				22	1	217	165	-16	4	410	395
5	6	406	411	-12	9	229	160	-24	0	321	291	24	1	243	221	-15	4	523	503
6	6	1072	1095	-11	9	1119	1132	-21	0	553	539	-24	2	327	364	-14	4	601	570
7	6	367	328	-10	9	332	341	-20	0	375	409	-22	2	244	234	-13	4	946	929
8	6	760	767	-7	9	868	888	-18	0	368	367	-21	2	536	528	-12	4	312	269
9	6	286	273	-6	9	739	731	-17	0	949	949	-18	2	557	580	-11	4	983	920
10	6	533	566	-2	9	467	468	-15	0	617	683	-17	2	225	166	-10	4	1498	1480
12	6	874	861	-1	9	1726	1742	-14	0	665	699	-16	2	982	946	-9	4	201	191
13	6	716	740	1	9	981	927												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 2*				5	6	599	612	-13	9	277	258	7	13	296	25[illegible]	-13	2	886	956
-8	4	359	327	6	6	419	421	-9	9	925	902	8	13	562	552	-12	2	1043	1329
-7	4	2817	2643	7	6	886	881	-8	9	885	912	-5	14	54C	544	-11	2	971	951
-5	4	1647	1628	8	6	646	629	-7	9	242	197	-2	14	495	541	-1C	2	885	849
-4	4	1037	986	9	6	419	445	-4	9	778	777	2	14	559	575	-8	2	644	637
-3	4	561	521	10	6	989	1033	-3	9	588	617	***K = 3****				-7	2	495	424
-2	4	737	727	11	6	256	221	-2	9	942	918	-22	0	345	319	-6	2	466	428
-1	4	662	651	12	6	491	522	-1	9	670	677	-20	0	682	696	-5	2	1676	1641
0	4	508	495	13	6	414	406	1	9	599	611	-19	0	496	485	-4	2	682	646
1	4	1606	1607	14	6	298	307	2	9	685	676	-18	0	250	195	-3	2	323	281
2	4	387	395	15	6	665	688	3	9	501	493	-16	0	208	144	-2	2	146	168
3	4	1315	1375	16	6	298	283	4	9	577	584	-15	0	724	727	-1	2	854	812
4	4	1355	1379	17	6	493	468	5	9	782	783	-14	0	559	552	0	2	1741	1718
5	4	799	822	18	6	416	381	6	9	785	774	-13	0	455	448	1	2	307	335
7	4	854	887	22	6	528	524	7	9	2C4	2C3	-11	0	1145	1151	2	2	797	846
8	4	769	817	-21	7	261	250	9	9	526	534	-10	0	1435	1455	3	2	497	514
9	4	830	920	-20	7	301	270	10	9	562	555	-8	0	991	1009	4	2	780	852
11	4	389	427	-17	7	407	388	12	9	585	550	-7	0	1113	1086	5	2	838	907
12	4	320	374	-15	7	492	498	15	9	221	236	-6	0	287	149	6	2	608	615
14	4	6C4	597	-13	7	367	328	16	9	278	169	-5	0	710	727	7	2	307	313
15	4	1098	1126	-12	7	611	600	18	9	712	678	-4	C	357	329	9	2	910	944
16	4	433	382	-11	7	523	504	-17	10	227	257	-3	C	1633	1657	1C	2	1291	1358
17	4	254	172	-9	7	721	711	-16	10	236	219	-2	0	726	723	11	2	347	380
18	4	282	284	-8	7	1070	1054	-12	10	833	838	-1	0	308	345	12	2	370	438
19	4	311	299	-7	7	764	782	-9	1C	594	648	1	0	304	345	14	2	397	425
20	4	565	580	-6	7	438	436	-3	10	387	395	2	0	726	723	15	2	253	246
21	4	290	223	-5	7	959	904	0	10	587	540	3	0	1628	1657	16	2	283	322
22	4	398	395	-4	7	663	660	1	10	580	582	4	0	334	329	17	2	4C4	398
-23	5	232	269	-3	7	578	598	2	10	801	797	5	C	725	727	18	2	367	380
-20	5	539	540	-2	7	519	525	3	10	261	245	7	0	1106	1086	19	2	880	598
-19	5	338	343	-1	7	687	679	5	10	472	457	8	0	989	1009	20	2	285	297
-18	5	217	232	0	7	327	353	7	10	493	540	10	0	1415	1455	22	2	464	448
-17	5	380	277	1	7	684	685	8	1C	542	532	11	0	1110	1151	24	2	227	209
-16	5	238	284	3	7	287	332	9	10	277	274	13	0	452	448	-22	3	324	278
-15	5	379	417	4	7	378	381	10	10	242	200	14	C	550	552	-19	3	424	43C
-14	5	480	489	6	7	307	309	12	1C	410	427	15	0	713	727	-18	3	569	557
-13	5	811	792	7	7	1160	1165	15	10	862	791	17	0	490	485	-17	3	857	611
-12	5	294	288	8	7	259	191	16	10	363	261	20	0	689	696	-16	3	842	882
-11	5	691	683	9	7	777	771	-13	11	344	395	22	0	318	319	-15	3	622	599
-10	5	1553	1472	11	7	256	248	-12	11	410	419	-23	1	255	292	-14	3	540	559
-8	5	1058	959	13	7	281	288	-9	11	574	604	-22	1	203	243	-12	3	408	413
-7	5	504	469	14	7	583	597	-8	11	453	461	-19	1	318	270	-11	3	841	826
-6	5	1075	1078	15	7	383	425	-6	11	824	808	-18	1	628	632	-9	3	739	715
-5	5	534	468	16	7	239	252	-5	11	281	212	-17	1	283	262	-8	3	1977	1885
-4	5	861	820	17	7	249	254	-4	11	276	306	-16	1	783	775	-7	3	771	732
-3	5	441	429	18	7	483	452	-2	11	303	335	-14	1	441	489	-6	3	307	304
-2	5	1232	121C	21	7	439	441	-1	11	468	489	-13	1	198	162	-5	3	767	734
-1	5	1036	976	-21	8	240	210	0	11	288	275	-12	1	177	159	-4	3	761	740
0	5	194	225	-20	8	437	448	2	11	527	525	-11	1	1435	1444	-3	3	335	353
1	5	1637	1620	-18	8	226	253	3	11	331	272	-10	1	279	279	-2	3	789	772
3	5	365	361	-17	8	345	354	4	11	375	353	-8	1	1226	1179	-1	3	3C9	293
4	5	1158	1210	-15	8	701	735	5	11	981	974	-7	1	958	944	0	3	760	736
7	5	682	699	-14	8	380	365	7	11	24C	225	-6	1	908	890	1	3	742	717
9	5	482	435	-13	8	355	361	8	11	457	486	-5	1	482	395	2	3	494	496
10	5	804	818	-12	8	813	811	9	11	325	303	-4	1	540	527	3	3	911	901
11	5	1446	1473	-11	8	947	967	10	11	288	274	-3	1	1241	1189	4	3	399	450
12	5	1598	1608	-10	8	720	705	11	11	257	230	-2	1	379	412	5	3	867	829
13	5	250	226	-8	8	716	690	12	11	257	274	-1	1	1376	1290	6	3	2526	2671
16	5	457	454	-7	8	671	660	-13	12	246	257	1	1	1595	1691	7	3	168	157
19	5	355	426	-6	8	482	413	-12	12	238	313	2	1	208	192	8	3	1140	1133
21	5	252	257	-4	8	672	612	-9	12	533	562	3	1	428	448	9	3	630	701
22	5	369	331	-2	8	384	387	-7	12	420	438	4	1	431	457	10	3	363	346
-20	6	868	679	0	8	959	952	-6	12	231	244	6	1	1045	1063	12	3	805	958
-18	6	280	291	1	8	990	982	-5	12	669	718	7	1	1227	1333	13	3	905	953
-14	6	631	575	2	8	306	317	-4	12	288	322	8	1	1066	11C4	14	3	281	273
-13	6	666	683	3	8	268	291	-2	12	471	479	9	1	693	712	15	3	368	319
-12	6	638	622	4	8	828	815	0	12	324	293	10	1	772	764	16	3	445	494
-11	6	319	316	5	8	622	643	2	12	435	473	11	1	433	448	18	3	358	363
-10	6	1077	1032	6	8	587	510	5	12	451	407	12	1	686	709	20	3	408	413
-9	6	1360	1307	7	8	433	420	6	12	240	245	13	1	285	281	22	3	549	542
-8	6	469	428	8	8	497	520	8	12	524	535	14	1	748	734	-23	4	3C8	338
-7	6	656	655	9	8	392	380	12	12	331	322	16	1	1316	1303	-21	4	310	382
-5	6	201	151	10	8	523	523	-1C	13	202	194	17	1	395	398	-20	4	513	476
-4	6	182	184	11	8	615	577	-9	13	299	338	18	1	356	367	-19	4	381	324
-3	6	376	348	12	8	485	463	-8	13	762	715	19	1	318	246	-18	4	482	502
-2	6	1828	1839	13	8	527	553	-7	13	194	211	22	1	457	431	-17	4	355	381
-1	6	158	152	15	8	983	1000	-2	13	352	398	-20	2	555	571	-15	4	1173	1149
0	6	351	368	17	8	346	324	-1	13	331	378	-19	2	548	549	-14	4	488	487
1	6	1097	1095	18	8	503	463	1	13	295	297	-17	2	386	400	-13	4	893	898
2	6	244	251	20	8	273	285	5	13	448	468	-15	2	718	708	-12	4	11C9	1069
3	6	445	452	-19	9	295	233	6	13	298	253	-14	2	911	884	-11	4	1038	992
4	6	1030	1054	-17	9	879	868												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 3*				2	6	1069	1047	3	9	261	235	-24	0	324	353	-10	2	507	499
-9	4	929	894	3	6	224	266	4	9	489	495	-23	0	199	145	-9	2	361	360
-8	4	1350	1272	4	6	451	408	5	9	867	858	-22	0	479	500	-8	2	416	413
-7	4	1202	1156	5	6	430	443	6	9	378	253	-21	0	287	348	-7	2	833	803
-6	4	613	575	6	6	604	620	7	9	575	569	-18	0	344	321	-6	2	250	243
-5	4	1960	1883	7	6	567	559	10	9	537	518	-15	0	337	375	-5	2	183	142
-4	4	888	825	8	6	1633	1047	11	9	420	467	-14	0	332	379	-4	2	857	838
-3	4	635	602	9	6	1189	1210	12	9	549	543	-13	0	646	653	-3	2	1868	1741
-2	4	885	870	12	6	689	725	14	9	440	445	-12	0	779	785	-2	2	170	157
-1	4	639	641	13	6	585	578	16	9	419	433	-11	0	800	793	-1	2	655	652
0	4	1015	1018	14	6	242	261	-17	10	304	306	-10	0	218	216	1	2	931	942
1	4	264	237	17	6	442	428	-16	10	368	364	-9	0	346	365	2	2	944	1027
2	4	1063	1087	19	6	253	209	-15	10	424	453	-7	0	970	936	3	2	1400	1480
3	4	1286	1252	20	6	377	348	-14	10	387	420	-5	0	338	344	4	2	547	556
4	4	163	145	21	6	372	349	-13	10	221	272	-4	0	1839	1879	5	2	1365	1415
6	4	804	810	-20	7	356	324	-12	10	326	285	-2	0	1436	1393	6	2	303	315
7	4	419	418	-19	7	376	350	-11	10	616	630	-1	0	255	207	7	2	313	328
8	4	234	243	-18	7	212	225	-10	10	474	510	0	0	556	545	8	2	288	275
9	4	1450	1488	-14	7	678	708	-9	10	226	147	1	0	208	207	10	2	1216	1217
10	4	721	721	-13	7	480	520	-8	10	407	419	2	0	1405	1393	11	2	963	995
11	4	489	453	-12	7	256	254	-7	10	445	441	4	0	1807	1879	12	2	643	664
12	4	267	205	-11	7	215	258	-3	10	420	437	5	0	349	344	13	2	506	506
13	4	301	344	-9	7	869	814	-2	10	547	533	6	0	206	73	14	2	381	384
15	4	347	377	-8	7	408	439	-1	10	671	675	7	0	962	936	15	2	475	491
16	4	330	350	-7	7	698	684	2	10	418	418	9	0	335	365	16	2	312	298
17	4	469	456	-6	7	225	186	3	10	408	395	10	0	181	216	17	2	397	381
18	4	280	315	-5	7	414	417	4	10	606	608	11	0	774	793	18	2	378	404
19	4	280	243	-4	7	675	651	5	10	301	251	12	0	743	785	19	2	334	328
20	4	572	578	-3	7	272	274	7	10	860	821	13	0	627	653	20	2	659	670
23	4	420	410	-2	7	1162	1155	8	10	367	375	14	0	354	379	21	2	234	204
-21	5	257	249	-1	7	630	590	9	10	535	514	15	0	362	375	23	2	260	298
-18	5	540	531	1	7	157	140	10	10	578	571	18	0	367	321	-23	3	211	207
-17	5	396	407	2	7	746	743	13	10	384	401	21	0	336	340	-21	3	356	361
-15	5	494	456	3	7	442	474	16	10	247	210	22	0	482	500	-19	3	625	625
-13	5	630	622	4	7	356	340	-15	11	256	261	24	0	332	354	-18	3	526	506
-12	5	1018	992	5	7	774	792	-14	11	781	832	-24	1	566	570	-17	3	333	339
-11	5	451	414	6	7	822	796	-12	11	244	277	-21	1	431	392	-16	3	626	621
-9	5	663	667	8	7	199	191	-11	11	387	389	-19	1	737	732	-15	3	693	674
-8	5	873	867	9	7	705	775	-10	11	265	247	-17	1	384	329	-13	3	374	371
-7	5	393	414	10	7	292	301	-8	11	957	955	-16	1	490	511	-12	3	439	398
-6	5	642	648	11	7	807	829	-7	11	233	225	-15	1	382	343	-11	3	858	882
-5	5	160	153	12	7	720	725	-6	11	609	641	-14	1	816	798	-10	3	1056	1017
-4	5	2130	1972	14	7	256	251	-5	11	263	250	-12	1	446	411	-9	3	977	968
-3	5	1720	1598	17	7	368	368	-4	11	370	349	-11	1	246	270	-8	3	561	476
-2	5	935	908	19	7	457	413	-3	11	381	390	-10	1	1034	1013	-6	3	1115	1005
-1	5	839	858	20	7	360	343	0	11	954	925	-9	1	1278	1205	-5	3	328	307
1	5	626	611	-20	8	262	337	1	11	831	798	-7	1	760	749	-4	3	793	784
2	5	637	634	-18	8	232	158	2	11	329	294	-6	1	1218	1215	-3	3	223	187
3	5	933	996	-17	8	508	561	4	11	482	522	-5	1	395	412	-1	3	2527	2436
5	5	1215	1232	-15	8	225	240	7	11	500	476	-4	1	869	835	0	3	563	559
6	5	2240	2293	-12	8	223	204	10	11	432	436	-3	1	561	523	1	3	517	517
7	5	195	203	-10	8	940	986	-12	12	481	537	-2	1	374	330	2	3	855	873
8	5	261	283	-9	8	236	185	-11	12	625	657	-1	1	913	820	3	3	453	456
9	5	685	683	-5	8	715	757	-9	12	266	278	0	1	645	648	4	3	1880	1908
10	5	516	509	-2	8	570	545	-8	12	229	196	1	1	1081	1109	5	3	813	852
11	5	456	428	-1	8	928	923	-7	12	209	198	2	1	480	479	6	3	870	899
12	5	491	502	2	8	648	653	-5	12	233	233	3	1	292	317	7	3	580	573
13	5	636	691	5	8	615	615	-3	12	684	712	4	1	807	836	8	3	1106	1153
14	5	338	324	6	8	218	275	-2	12	743	779	5	1	581	596	9	3	374	394
16	5	236	154	8	8	1111	1117	0	12	545	559	6	1	1856	1651	11	3	198	170
17	5	419	399	9	8	1049	1064	2	12	355	278	7	1	780	770	12	3	215	181
18	5	309	328	10	8	331	307	3	12	566	589	8	1	722	739	13	3	499	470
19	5	367	364	12	8	296	277	4	12	356	408	9	1	1194	1220	14	3	1155	1137
20	5	580	587	13	8	489	445	6	12	307	297	10	1	622	648	15	3	386	402
21	5	408	397	14	8	330	322	7	12	503	490	12	1	219	207	19	3	491	490
-22	6	329	338	15	8	228	288	11	12	497	562	14	1	812	818	22	3	345	327
-18	6	503	484	16	8	257	178	-8	13	309	351	15	1	619	626	23	3	219	216
-17	6	409	410	17	8	488	435	-6	13	457	493	16	1	927	942	-22	4	285	322
-15	6	764	753	-19	9	461	487	-4	13	267	247	18	1	375	327	-21	4	366	396
-14	6	248	245	-18	9	304	318	-3	13	460	456	19	1	451	456	-20	4	277	345
-13	6	232	214	-15	9	209	220	-2	13	261	262	20	1	361	411	-19	4	364	319
-12	6	988	963	-14	9	804	849	-1	13	298	296	21	1	753	760	-18	4	703	695
-10	6	613	591	-13	9	621	604	0	13	462	479	22	1	292	251	-17	4	709	702
-8	6	1041	978	-12	9	522	516	1	13	348	334	23	1	486	509	-16	4	703	704
-7	6	392	414	-9	9	357	312	3	13	520	505	-22	2	275	328	-14	4	873	867
-6	6	644	647	-8	9	220	188	5	13	345	366	-18	2	497	517	-13	4	1387	1369
-5	6	919	882	-5	9	358	339	6	13	276	243	-15	2	280	260	-12	4	286	215
-3	6	390	359	-4	9	768	772	-1	14	182	98	-14	2	645	657	-8	4	346	323
-2	6	298	298	-2	9	489	483	0	14	404	404	-13	2	1339	1353	-7	4	1843	1728
-1	6	1121	1141	-1	9	268	255	1	14	246	302	-12	2	980	982	-6	4	919	875
0	6	510	523	1	9	262	205	***K = 4****				-11	2	683	681	-5	4	818	858
1	6	318	267	2	9	766	730												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 4**				17	6	372	382	-4	10	528	546	16	0	523	540	-11	3	350	394
-4	4	1769	1702	18	6	348	279	-3	10	418	405	17	0	275	261	-9	3	576	539
-3	4	998	927	21	6	303	263	0	10	439	417	18	0	235	275	-8	3	393	404
-2	4	961	964	-21	7	540	561	1	10	297	315	19	0	263	206	-7	3	1101	1136
-1	4	662	621	-20	7	251	291	2	10	277	282	20	0	677	721	-6	3	530	587
0	4	240	250	-18	7	387	370	3	10	629	591	-23	1	346	361	-4	3	1107	1047
1	4	1478	1490	-17	7	212	175	5	10	736	762	-22	1	256	272	-3	3	2155	2030
2	4	1908	1855	-14	7	426	480	6	10	541	595	-17	1	678	660	-2	3	845	807
4	4	876	915	-13	7	259	176	7	10	484	489	-16	1	328	315	-1	3	317	288
5	4	500	535	-12	7	515	506	8	10	269	252	-15	1	732	729	0	3	1413	1401
6	4	1507	1535	-11	7	766	736	9	10	288	347	-14	1	475	466	1	3	861	887
7	4	1442	1463	-10	7	442	451	12	10	210	176	-13	1	284	311	3	3	298	326
8	4	215	212	-9	7	253	232	14	10	299	232	-12	1	404	388	4	3	563	624
9	4	251	240	-7	7	289	319	15	10	456	455	-10	1	779	770	5	3	343	342
10	4	619	640	-6	7	609	618	-15	11	364	391	-8	1	1083	1079	6	3	950	976
11	4	1053	1092	-5	7	741	734	-14	11	213	170	-7	1	1140	1153	7	3	287	306
12	4	432	454	-4	7	409	365	-13	11	419	453	-6	1	636	642	8	3	353	384
14	4	388	371	-3	7	534	548	-12	11	638	669	-5	1	937	948	9	3	301	335
15	4	565	586	2	7	661	694	-8	11	270	303	-4	1	967	919	10	3	195	200
16	4	986	961	4	7	858	879	-7	11	323	339	-3	1	1923	1861	11	3	380	353
17	4	442	438	5	7	834	830	-6	11	536	560	-2	1	331	357	12	3	989	929
18	4	464	417	6	7	276	266	-5	11	232	240	0	1	157	91	13	3	274	257
19	4	244	207	7	7	584	556	-4	11	300	320	2	1	1077	1153	14	3	281	211
21	4	218	204	8	7	444	420	-3	11	292	292	3	1	924	1024	15	3	617	624
-20	5	323	371	9	7	605	639	-1	11	609	602	4	1	718	743	16	3	980	964
-19	5	538	527	12	7	340	289	1	11	219	156	6	1	931	958	21	3	320	283
-16	5	358	281	13	7	556	575	2	11	944	946	7	1	538	573	22	3	239	324
-15	5	215	182	17	7	290	329	3	11	279	310	8	1	800	834	-21	4	210	241
-14	5	573	565	19	7	411	378	6	11	364	332	9	1	704	721	-20	4	769	755
-11	5	1119	1075	-18	8	275	286	7	11	581	548	10	1	693	782	-17	4	884	855
-10	5	1362	1310	-17	8	536	554	8	11	611	595	12	1	839	825	-15	4	1235	1226
-9	5	262	262	-15	8	428	493	11	11	243	213	14	1	280	326	-14	4	901	903
-8	5	207	161	-14	8	422	459	13	11	240	190	15	1	331	330	-12	4	401	405
-6	5	868	842	-12	8	383	392	-10	12	530	550	16	1	398	396	-9	4	298	242
-5	5	340	389	-8	8	888	875	-9	12	252	280	17	1	705	751	-7	4	633	596
-4	5	868	838	-7	8	275	294	-5	12	332	309	20	1	286	278	-6	4	1201	1176
-2	5	948	984	-5	8	198	213	-4	12	541	565	22	1	365	307	-5	4	1242	1125
-1	5	2274	2176	-4	8	858	832	-3	12	316	347	23	1	570	587	-4	4	191	153
0	5	347	357	-3	8	421	387	-1	12	509	506	-23	2	311	288	-3	4	431	427
1	5	1440	1451	-1	8	219	202	0	12	327	306	-20	2	492	493	-2	4	871	871
2	5	592	614	1	8	426	460	1	12	294	333	-17	2	323	328	0	4	2098	2032
3	5	1402	1428	2	8	1225	1229	2	12	362	397	-15	2	487	508	1	4	761	713
4	5	1713	1735	6	8	640	626	4	12	737	739	-13	2	843	835	2	4	733	735
8	5	852	842	7	8	1179	1202	5	12	679	667	-12	2	203	175	3	4	1120	1174
9	5	349	346	9	8	268	218	-8	13	260	269	-11	2	459	468	4	4	317	330
11	5	258	271	10	8	462	496	-7	13	316	363	-10	2	224	223	5	4	611	641
12	5	709	735	11	8	286	336	-2	13	432	440	-9	2	226	225	6	4	301	308
13	5	585	583	12	8	324	366	-1	13	562	608	-7	2	171	164	7	4	872	861
14	5	464	465	13	8	250	237	1	13	593	546	-6	2	1336	1303	8	4	1029	1045
15	5	241	133	14	8	318	331	2	13	494	460	-5	2	1465	1420	9	4	233	248
17	5	421	437	15	8	522	498	5	13	289	288	-4	2	986	996	10	4	427	448
18	5	247	269	16	8	240	231	7	13	257	275	-3	2	522	512	12	4	195	198
19	5	639	635	17	8	275	218	**K = 5****				-2	2	758	788	13	4	939	970
21	5	211	202	-14	9	262	269	-23	0	237	274	-1	2	763	736	14	4	512	471
22	5	339	374	-13	9	231	304	-20	0	719	721	0	2	911	962	15	4	885	888
-22	6	278	281	-12	9	849	852	-19	0	248	298	1	2	469	475	17	4	452	444
-17	6	472	458	-11	9	593	587	-18	0	272	275	2	2	584	586	18	4	694	670
-16	6	261	197	-10	9	397	360	-17	0	265	241	3	2	1084	1193	19	4	229	192
-15	6	471	469	-9	9	307	290	-16	0	529	540	4	2	245	242	21	4	366	309
-13	6	1072	1040	-8	9	207	88	-15	0	265	264	5	2	856	919	22	4	204	205
-9	6	620	613	-7	9	229	232	-13	0	796	783	6	2	889	910	-18	5	753	748
-8	6	826	796	-6	9	388	404	-11	0	358	340	7	2	1359	1403	-17	5	726	756
-7	6	842	804	-2	9	277	296	-10	0	531	517	8	2	984	912	-16	5	241	174
-6	6	421	405	-1	9	278	306	-9	0	360	319	9	2	675	691	-13	5	404	372
-5	6	660	653	1	9	297	195	-8	0	392	364	10	2	838	905	-12	5	934	876
-4	6	254	206	2	9	838	815	-7	0	360	402	11	2	216	224	-10	5	364	360
-2	6	344	367	3	9	527	522	-6	0	1813	1829	13	2	379	392	-9	5	932	901
-1	6	714	687	4	9	890	908	-5	0	2028	2114	15	2	497	487	-7	5	193	223
0	6	875	852	5	9	692	682	-3	0	528	517	18	2	606	628	-6	5	463	489
1	6	1074	1070	6	9	433	441	-1	0	667	649	19	2	678	671	-5	5	468	487
2	6	992	987	7	9	221	235	1	0	687	649	20	2	756	782	-4	5	806	781
3	6	485	505	9	9	880	875	3	0	616	617	21	2	307	295	-3	5	1160	1094
5	6	226	260	10	9	412	447	5	0	2028	2114	-22	3	275	279	-2	5	724	683
6	6	693	665	11	9	435	456	6	0	1809	1829	-21	3	217	173	-1	5	351	360
7	6	812	871	12	9	595	621	7	0	358	402	-20	3	272	283	0	5	577	586
10	6	552	560	13	9	288	268	8	0	378	364	-19	3	518	487	1	5	403	385
11	6	357	368	-17	10	201	239	9	0	328	319	-18	3	412	476	2	5	719	769
12	6	278	213	-15	10	307	328	10	0	526	517	-17	3	1035	1026	3	5	499	528
13	6	231	252	-12	10	238	253	11	0	352	340	-15	3	478	455	4	5	180	189
14	6	222	229	-11	10	233	278	13	0	796	783	-13	3	236	223	5	5	595	622
15	6	337	270	-10	10	467	435	15	0	228	264	-12	3	622	647	6	5	760	776
16	6	640	647	-9	10	705	783												

Table 31 (continued)

```
   H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL
  ***K =   5****          0   8  1039  1006     -5  13   247   213    -10   2   718   695      5   4   686   713
   7   5   342   336      4   8   668   694     -2  13   422   375     -9   2   373   315      6   4   248   263
   9   5   610   633      5   8   832   823     -1  13   373   400     -7   2   716   702      7   4   318   369
  11   5   779   792      7   8   539   515      0  13   356   351     -6   2   277   239      8   4   332   362
  12   5   663   636      8   8   820   808      1  13   297   299     -5   2   217   203      9   4   345   364
  14   5   663   686      9   8   308   277      2  13   334   322     -4   2   641   689     10   4   790   790
  16   5   959   918     11   8   475   450      5  13   354   348     -3   2  1332  1319     11   4   398   424
  17   5   395   402     13   8   650   638     ***K =   6****         -2   2   813   770     13   4   828   847
  18   5   388   351     14   8   318   330    -22   0   370   381     -1   2   665   646     14   4   536   526
  20   5   696   682     18   8   449   397    -21   0   369   391      1   2   374   360     16   4   582   546
  21   5   212   183    -16   9   362   393    -20   0   255   235      2   2   866   898     17   4  1006   971
 -21   6   282   322    -15   9   369   384    -18   0   349   374      3   2   704   730     19   4   565   526
 -19   6   258   227    -12   9   434   433    -15   0   369   354      4   2   934   948    -21   5   261   285
 -16   6   296   336    -10   9   664   647    -14   0   727   736      5   2   976  1036    -19   5   275   255
 -15   6   570   583     -8   9   639   603    -13   0   925   888      6   2   200   175    -16   5   761   742
 -14   6   463   481     -7   9   261   298    -12   0   586   598      8   2   222   267    -15   5   428   410
 -13   6   434   435     -5   9   588   577    -11   0   925   871      9   2   440   482    -14   5   760   802
 -10   6   392   396     -4   9   845   837     -9   0  1142  1140     11   2   433   392    -11   5  1213  1145
  -9   6   570   522     -3   9   481   413     -8   0   204   160     12   2  1009  1066    -10   5   355   365
  -8   6   478   467      0   9   261   182     -7   0  1072  1103     13   2   992  1021     -9   5   352   365
  -7   6   428   418      2   9   625   640     -6   0   370   369     14   2   260   217     -8   5   644   632
  -6   6   683   677      3   9   672   675     -5   0   612   634     15   2   593   606     -6   5   222   223
  -3   6   675   649      4   9   554   595     -4   0   693   651     16   2   514   538     -5   5   391   396
  -2   6   221   241      5   9   404   417     -3   0   847   858     17   2   676   698     -4   5   958   927
  -1   6   857   864      6   9   325   341     -1   0   704   684     18   2   297   308     -3   5   674   662
   0   6  1253  1258      8   9   480   508      0   0   669   650     20   2   262   286     -2   5   662   631
   1   6   448   422      9   9   499   487      1   0   671   684     22   2   283   273     -1   5   923   928
   3   6   416   397     10   9   456   428      3   0   814   858    -22   3   332   335      1   5   285   289
   4   6   448   428     11   9   681   701      4   0   685   651    -18   3   420   418      2   5   703   686
   5   6   505   479     12   9   328   338      5   0   616   634    -16   3   818   823      3   5   770   809
   6   6   476   444     16   9   337   312      6   0   360   369    -15   3   248   291      4   5   292   296
   8   6   918   908    -16  10   241   293      7   0  1086  1103    -14   3   613   611      5   5   472   499
   9   6   364   371    -13  10   434   480      8   0   217   160    -13   3   425   442      6   5   385   363
  10   6   236   228    -12  10   426   433      9   0  1124  1140    -11   3   484   471      9   5   498   402
  11   6   312   292    -11  10   431   432     11   0   878   871    -10   3   481   496     10   5   241   218
  14   6   243   229    -10  10   337   351     12   0   605   598     -9   3   850   883     11   5   396   361
  15   6   494   918     -8  10   344   392     13   0   866   888     -8   3   259   230     12   5   290   240
  16   6   278   235     -7  10   377   390     14   0   722   736     -7   3   469   458     13   5   562   612
  17   6   487   483     -5  10   580   584     15   0   396   354     -6   3   185   152     14   5   767   752
  18   6   457   420     -2  10   899   882     18   0   351   374     -4   3  1258  1170     15   5   222   134
 -20   7   270   260     -1  10   490   529     20   0   230   235     -3   3   176   158     16   5  1040  1035
 -18   7   254   263      0  10   819   825     21   0   396   391     -2   3   246   260     17   5   364   279
 -17   7   347   343      1  10   726   685     22   0   389   381     -1   3  1630  1539     19   5   212   204
 -16   7   247   273      2  10   226   204    -22   1   349   345      0   3   978   942     20   5   254   224
 -15   7   864   870      7  10   953   950    -19   1   225   213      1   3   391   352    -19   6   290   305
 -12   7   959   926      8  10   906   908    -18   1   413   407      2   3  1507  1481    -17   6   277   297
 -10   7   481   414     12  10   241   253    -14   1   959   963      3   3   218   222    -13   6   535   546
  -8   7   286   279     13  10   481   485    -13   1   393   378      4   3   439   448    -11   6   423   426
  -6   7   320   301     14  10   322   307    -12   1   814   809      5   3   502   530    -10   6   475   455
  -5   7   678   692    -16  11   415   442    -11   1   896   879      6   3   470   515     -9   6   594   587
  -4   7  1202  1278    -13  11   235   194     -9   1   520   524      7   3   342   350     -8   6   651   648
  -3   7   501   477     -9  11   332   317     -8   1   189   135      9   3   339   353     -6   6   208   122
  -1   7   238   233     -8  11   324   313     -7   1   679   671     11   3   283   284     -5   6  1225  1213
   1   7   278   280     -7  11   256   245     -6   1  1150  1142     12   3   567   613     -4   6   393   406
   2   7   832   853     -5  11   460   474     -5   1   261   271     13   3   836   868     -1   6   528   524
   3   7   304   307     -4  11   923   918     -4   1   904   977     14   3   853   849      0   6   409   412
   5   7   400   395     -2  11   470   452     -3   1   296   236     16   3   622   660      1   6   534   479
   6   7   688   698     -1  11   341   326     -1   1   482   485     18   3   262   267      2   6   663   676
   7   7   307   340      1  11   701   713      0   1   698   702     20   3   426   425      3   6   597   587
   8   7   483   481      4  11   721   735      1   1   508   529    -21   4   335   346      4   6   305   354
   9   7   537   507      5  11   321   292      2   1   991  1009    -20   4   233   210      5   6   513   544
  11   7   717   710      6  11   203   204      3   1   352   384    -19   4   706   729      8   6   624   609
  14   7   477   483      7  11   235   182      4   1  1467  1550    -18   4   247   219      9   6   641   635
  17   7   228   171      9  11   491   520      5   1   316   329    -17   4   501   539     12   6   463   467
  19   7   227   218     10  11   202   279      6   1  1924  1941    -16   4   277   215     13   6   719   733
 -18   8   295   271     11  11   203   208      7   1   388   440    -12   4   405   365     14   6   340   373
 -17   8   297   289     12  11   235   247      8   1   931   965    -11   4   624   602     15   6   424   391
 -16   8   217   235    -11  12   285   288      9   1   440   446     -9   4   484   481     16   6   284   298
 -14   8   531   586     -6  12   259   247     10   1   731   772     -8   4   483   515     17   6   446   432
 -13   8   563   568     -5  12   461   499     11   1   524   856     -6   4   532   558     18   6   953   962
 -12   8   314   349     -3  12   378   387     13   1   237   191     -4   4   343   348    -19   7   285   230
 -11   8   267   221     -2  12   663   687     14   1   706   752     -3   4   882   849    -18   7   273   323
 -10   8   328   317     -1  12   236   255     15   1   593   608     -2   4   592   550    -17   7   257   265
  -7   8  1021  1026      1  12   397   435     18   1   660   623     -1   4  1617  1588    -16   7   255   298
  -6   8   378   328      2  12   444   428     20   1   326   355      0   4   519   508    -14   7   596   592
  -5   8   595   580      3  12   839   867    -22   2   356   318      1   4   517   506    -13   7   237   245
  -4   8   567   538      6  12   232   219    -19   2   256   301      2   4   977   976     -9   7   253   253
  -2   8   358   568      7  12   301   320    -18   2   755   767      3   4   259   260     -8   7  1188  1173
  -1   8   368   380     -6  13   239   281    -12   2   919   912      4   4   253   294
```

Table 31 (continued)

H	L	FOBS	FCAL
***K =		6****	
-7	7	584	570
-6	7	1180	1176
-5	7	258	73
-2	7	848	854
-1	7	612	635
0	7	417	402
1	7	340	366
2	7	272	295
3	7	496	527
4	7	418	409
5	7	401	422
6	7	783	803
7	7	344	357
8	7	234	198
10	7	422	393
12	7	492	501
14	7	270	276
15	7	481	389
16	7	554	554
-17	8	315	287
-13	8	249	268
-11	8	800	771
-10	8	520	516
-9	8	623	606
-8	8	419	410
-7	8	465	432
-6	8	767	719
-5	8	853	811
-3	8	827	815
-2	8	211	62
-1	8	347	339
0	8	277	277
2	8	732	718
3	8	541	538
4	8	434	442
7	8	457	445
9	8	688	692
10	8	348	327
11	8	835	834
15	8	452	448
16	8	412	382
-14	9	464	448
-12	9	222	242
-10	9	333	289
-9	9	342	354
-8	9	714	720
-6	9	1279	1303
-5	9	527	497
-4	9	570	562
-2	9	448	431
0	9	327	364
3	9	233	231
4	9	287	358
5	9	459	504
6	9	750	732
8	9	458	449
12	9	484	485
13	9	401	391
14	9	448	481
-15	10	272	267
-11	10	252	261
-9	10	392	372
-8	10	592	591
-7	10	737	720
-4	10	317	314
-3	10	698	689
0	10	290	334
1	10	222	83
2	10	291	270
3	10	656	661
4	10	283	295
5	10	500	542
6	10	376	374
9	10	453	460
11	10	532	540
12	10	246	260
13	10	198	197
-12	11	235	262
-10	11	276	283
-7	11	323	363
-6	11	347	378
-5	11	218	258
-4	11	363	394
-2	11	674	688
-1	11	452	455
0	11	466	473
2	11	406	399
3	11	225	218
4	11	220	238
6	11	439	417
7	11	391	382
8	11	280	321
9	11	270	289
10	11	315	323
11	11	219	224
-8	12	241	229
-7	12	390	380
-5	12	373	334
-4	12	320	341
-3	12	611	648
-2	12	252	200
-1	12	580	584
1	12	236	239
4	12	502	471
5	12	303	279
7	12	234	234
***K =		7****	
-21	0	482	534
-17	0	585	592
-15	0	632	683
-14	0	284	303
-13	0	671	648
-12	0	324	280
-8	0	678	698
-7	0	1481	1515
-6	0	256	250
-5	0	933	938
-4	0	447	452
-3	0	378	399
-2	0	509	477
-1	0	1538	1488
1	0	1455	1488
2	0	555	477
3	0	483	399
4	0	425	452
5	0	940	938
6	0	271	250
7	0	1446	1515
8	0	698	698
12	0	284	280
13	0	639	648
14	0	291	303
15	0	653	683
17	0	597	592
21	0	486	534
-20	1	561	590
-19	1	332	257
-16	1	614	585
-14	1	577	543
-13	1	463	474
-12	1	508	488
-10	1	908	898
-8	1	672	606
-7	1	546	593
-6	1	725	776
-5	1	524	536
-4	1	1354	1339
-2	1	948	942
-1	1	470	451
0	1	387	391
2	1	241	225
3	1	214	190
4	1	1947	2023
5	1	882	952
7	1	366	402
8	1	414	468
9	1	698	744
10	1	940	949
12	1	1030	1076
13	1	234	184
14	1	626	604
18	1	284	329
19	1	252	280
20	1	327	303
21	1	219	217
-19	2	268	183
-18	2	312	317
-17	2	836	861
-16	2	290	250
-15	2	270	207
-11	2	209	107
-10	2	508	511
-9	2	646	623
-7	2	762	743
-6	2	337	294
-5	2	950	893
-4	2	791	761
-3	2	1707	1622
-2	2	401	382
-1	2	611	802
1	2	584	627
2	2	476	506
3	2	364	365
4	2	425	475
5	2	163	166
6	2	527	528
7	2	1174	1176
8	2	209	207
9	2	264	227
10	2	726	758
11	2	337	347
12	2	302	288
13	2	508	521
14	2	373	398
15	2	1025	1050
18	2	304	265
20	2	256	132
21	2	434	379
-20	3	476	523
-19	3	246	312
-16	3	484	487
-15	3	248	234
-14	3	714	748
-11	3	510	498
-8	3	484	508
-7	3	803	867
-6	3	1281	1235
-5	3	380	223
-4	3	902	939
-3	3	354	297
-2	3	374	338
0	3	864	844
1	3	196	182
2	3	385	380
4	3	850	876
6	3	191	137
7	3	461	485
9	3	293	346
10	3	813	836
12	3	443	458
13	3	246	212
16	3	367	386
18	3	526	544
19	3	237	197
-19	4	305	317
-17	4	820	821
-15	4	628	617
-13	4	405	445
-11	4	256	237
-9	4	716	663
-8	4	253	269
-6	4	248	284
-3	4	1011	980
-2	4	690	665
-1	4	275	287
0	4	466	473
1	4	324	339
2	4	318	322
3	4	580	585
4	4	285	321
5	4	319	303
6	4	232	223
7	4	894	900
8	4	373	348
10	4	365	351
11	4	287	311
13	4	533	564
15	4	1090	1106
16	4	335	376
19	4	248	234
20	4	278	256
-20	5	248	282
-19	5	333	345
-16	5	483	489
-14	5	658	637
-12	5	257	277
-11	5	406	417
-10	5	438	431
-9	5	414	400
-8	5	783	745
-6	5	714	679
-5	5	826	834
-2	5	480	459
-1	5	376	320
0	5	794	796
1	5	249	197
2	5	376	387
3	5	277	278
4	5	223	190
5	5	326	307
7	5	383	355
8	5	258	251
10	5	679	667
14	5	538	567
15	5	327	318
16	5	376	398
18	5	796	779
19	5	203	145
-19	6	339	315
-17	6	416	402
-16	6	354	353
-15	6	583	580
-13	6	401	402
-10	6	228	226
-9	6	628	579
-8	6	223	138
-7	6	822	828
-5	6	268	272
-4	6	505	512
-3	6	1013	982
-2	6	584	548
0	6	382	375
2	6	264	198
3	6	876	857
5	6	868	862
6	6	235	241
7	6	328	347
11	6	674	694
12	6	290	258
13	6	255	266
15	6	663	638
17	6	443	458
-16	7	719	704
-14	7	483	482
-13	7	378	373
-12	7	329	353
-10	7	834	835
-9	7	240	182
-8	7	784	677
-7	7	675	701
-6	7	767	757
-4	7	783	751
-3	7	316	316
-2	7	618	569
-1	7	227	206
0	7	652	624
1	7	226	201
2	7	393	385
3	7	326	274
4	7	247	251
8	7	971	978
10	7	218	165
12	7	309	281
13	7	420	390
14	7	518	497
16	7	282	282
17	7	324	286
-16	8	295	286
-15	8	237	221
-13	8	725	730
-12	8	285	296
-9	8	335	327
-7	8	1082	976
-6	8	341	341
-5	8	936	967
-4	8	556	540
-3	8	344	346
-2	8	379	406
-1	8	322	318
0	8	431	414
1	8	596	588
3	8	945	952
6	8	267	283
7	8	293	175
9	8	404	424
10	8	511	499
11	8	501	514
13	8	439	422
-10	9	577	551
-9	9	367	393
-8	9	783	801
-7	9	276	197
-4	9	647	624
-3	9	287	263
-2	9	764	748
1	9	438	381
4	9	644	635
8	9	472	459
10	9	414	386
11	9	359	350
12	9	580	577
13	9	272	273
14	9	288	262
-13	10	372	448
-10	10	308	335
-9	10	308	312
-7	10	348	353
-6	10	216	171
-5	10	862	862
-3	10	280	264
-2	10	431	436
1	10	[illegible]	603
5	10	335	286
7	10	333	351
8	10	251	258
9	10	300	325
11	10	285	285
-8	11	201	218
-2	11	602	638
4	11	397	401
8	11	318	315
9	11	207	233
-5	12	628	677
-4	12	488	420
1	12	481	510
3	12	204	152
***K =		8****	
-15	0	1050	1043
-14	0	206	217
-13	0	362	354
-9	0	990	987
-7	0	203	179
-6	0	205	164
-5	0	880	905
-4	0	483	498
-3	0	984	1019
-2	0	551	554
-1	0	851	796
1	0	775	796
2	0	858	856
3	0	984	1019
4	0	488	498
6	0	913	905
7	0	213	179
9	0	984	987
13	0	370	354
14	0	274	217
15	0	1034	1043
-18	1	478	510
-16	1	227	248
-12	1	1056	1060
-7	1	576	578
-6	1	1419	1302
-5	1	448	463
-4	1	725	695
-3	1	238	216
-2	1	664	622
-1	1	422	371
2	1	1215	1290
4	1	240	282

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 8*				8	4	578	625	7	8	252	275	-14	2	297	365	11	5	285	322
5	1	282	232	9	4	603	676	8	8	229	219	-11	2	597	582	-15	6	324	347
6	1	621	837	10	4	312	377	9	8	448	463	-10	2	230	175	-14	6	269	286
7	1	384	411	11	4	275	306	11	8	282	283	-9	2	585	584	-13	6	459	469
8	1	653	647	13	4	735	748	12	8	374	350	-8	2	399	416	-12	6	283	268
10	1	457	505	14	4	320	355	13	8	455	432	-7	2	544	546	-11	6	376	408
12	1	826	864	15	4	396	418	-10	9	328	351	-6	2	384	375	-10	6	415	446
13	1	437	442	16	4	387	360	-9	9	298	327	-5	2	515	519	-9	6	442	423
14	1	392	388	17	4	248	242	-8	9	743	767	-4	2	255	238	-7	6	282	282
17	1	231	212	19	4	281	188	-7	9	295	285	-3	2	731	685	-6	6	255	227
18	1	382	293	-16	5	292	327	-6	9	396	404	0	2	632	658	-4	6	249	205
20	1	288	275	-15	5	493	496	-4	9	337	314	1	2	215	188	-3	6	749	720
-19	2	470	471	-12	5	259	289	-1	9	306	239	3	2	452	478	0	6	420	421
-18	2	396	378	-8	5	909	883	0	9	620	582	5	2	494	468	2	6	378	319
-17	2	480	495	-4	5	513	506	2	9	669	653	7	2	1019	1083	3	6	676	673
-16	2	305	342	-3	5	635	608	5	9	252	225	10	2	455	461	5	6	1185	1165
-15	2	731	736	-1	5	819	781	6	9	730	726	13	2	435	446	6	6	265	174
-11	2	385	324	0	5	219	197	9	9	287	271	15	2	396	373	7	6	384	359
-10	2	290	175	1	5	827	838	11	9	214	192	17	2	225	208	8	6	595	611
-9	2	760	768	2	5	1179	1196	-11	10	268	344	-17	3	432	448	11	6	677	685
-8	2	289	323	3	5	322	320	-10	10	207	228	-16	3	369	390	14	6	246	286
-7	2	552	532	4	5	491	465	-8	10	208	200	-14	3	849	873	15	6	287	323
-6	2	384	376	8	5	785	814	-7	10	639	646	-12	3	289	321	-14	7	283	281
-3	2	722	693	10	5	490	494	-5	10	411	395	-11	3	240	238	-12	7	278	305
-2	2	441	460	12	5	233	282	-3	10	416	460	-10	3	355	328	-10	7	466	423
-1	2	907	914	13	5	224	236	-1	10	303	368	-9	3	273	267	-8	7	718	719
3	2	475	497	15	5	217	235	1	10	336	348	-8	3	482	476	-5	7	318	337
4	2	286	304	16	5	783	687	3	10	519	496	-7	3	550	566	-4	7	220	172
5	2	1049	1111	17	5	252	301	9	10	465	417	-6	3	1265	1211	-1	7	312	285
7	2	223	261	18	5	315	292	-8	11	289	301	-5	3	446	388	0	7	295	341
9	2	771	819	-17	6	322	269	-4	11	458	498	-4	3	293	255	2	7	688	684
10	2	348	311	-12	6	660	660	-1	11	231	117	-3	3	639	600	3	7	467	482
12	2	388	402	-11	6	769	799	0	11	234	163	-2	3	530	515	4	7	537	471
13	2	689	663	-5	6	586	542	4	11	293	257	0	3	383	382	5	7	326	308
14	2	219	91	-4	6	578	582	6	11	720	706	1	3	264	278	6	7	477	459
15	2	356	362	-3	6	292	223	***K = 9****				2	3	670	669	8	7	645	660
17	2	269	271	-2	6	532	536	-17	0	740	753	4	3	626	638	11	7	391	377
-16	3	465	484	-1	6	617	605	-14	0	279	295	5	3	529	539	13	7	205	221
-15	3	348	390	0	6	274	236	-13	0	790	802	6	3	341	283	14	7	479	492
-14	3	757	739	2	6	286	315	-11	0	414	385	7	3	221	219	-13	8	605	663
-13	3	336	273	3	6	1089	1085	-10	0	406	363	10	3	513	508	-5	8	545	514
-12	3	869	867	5	6	962	968	-9	0	265	293	12	3	511	543	-3	8	671	678
-10	3	221	195	7	6	839	828	-7	0	958	951	13	3	312	289	-1	8	341	340
-9	3	271	245	9	6	441	453	-6	0	433	489	15	3	237	274	1	8	864	829
-8	3	684	648	10	6	278	303	-5	0	281	319	-14	4	379	396	5	8	729	767
-6	3	497	481	12	6	429	486	-3	0	496	463	-12	4	494	453	6	8	261	230
-5	3	295	304	13	6	767	775	-1	0	859	854	-11	4	544	544	8	8	384	413
-4	3	916	884	-16	7	378	410	1	0	796	884	-9	4	613	588	11	8	428	413
-3	3	325	347	-14	7	781	812	3	0	646	663	-8	4	269	279	-8	9	253	261
-2	3	292	299	-8	7	951	965	5	0	287	319	-6	4	699	703	-6	9	231	255
-1	3	560	512	-6	7	333	307	6	0	496	499	-4	4	424	444	-2	9	501	508
0	3	1635	1622	-5	7	307	400	7	0	932	951	-3	4	876	875	3	9	228	244
1	3	391	421	-4	7	326	378	8	0	209	187	-2	4	285	275	4	9	581	603
2	3	1629	1618	-2	7	687	579	10	0	375	363	-1	4	393	376	6	9	311	329
6	3	351	365	0	7	736	732	11	0	406	385	0	4	1160	1150	-5	10	422	417
8	3	473	512	2	7	541	520	13	0	790	802	1	4	333	378	-2	10	251	250
10	3	313	382	3	7	348	382	14	0	304	295	2	4	625	672	1	10	383	348
12	3	582	623	4	7	583	567	17	0	749	753	5	4	568	537	3	10	329	276
14	3	535	534	5	7	462	458	-17	1	373	401	7	4	901	996	5	10	318	331
16	3	412	399	6	7	1088	1064	-14	1	801	806	8	4	444	419	***K = 10****			
17	3	233	236	7	7	450	482	-12	1	308	312	11	4	396	394	-17	0	271	286
18	3	288	277	8	7	303	294	-10	1	309	323	14	4	261	224	-15	0	724	749
-19	4	296	274	9	7	362	372	-8	1	484	366	15	4	298	272	-14	0	462	455
-18	4	392	415	10	7	297	322	-7	1	484	456	17	4	233	216	-13	0	311	339
-17	4	620	629	14	7	344	358	-6	1	825	813	-17	5	404	390	-12	0	634	633
-16	4	279	292	15	7	303	333	-5	1	251	281	-16	5	328	358	-5	0	463	450
-15	4	229	291	16	7	762	737	-4	1	1314	1301	-14	5	681	577	-3	0	692	703
-12	4	216	137	-15	8	496	508	-3	1	378	365	-13	5	226	162	-2	0	341	336
-11	4	586	575	-14	8	229	176	-2	1	487	426	-12	5	515	527	2	0	305	334
-9	4	482	467	-12	8	264	298	0	1	498	516	-9	5	290	272	3	0	664	703
-8	4	262	215	-11	8	712	708	2	1	418	483	-6	5	759	721	5	0	443	450
-5	4	277	221	-8	8	350	353	3	1	318	351	-4	5	238	169	9	0	228	231
-4	4	278	283	-7	8	364	393	4	1	1248	1297	-3	5	541	522	12	0	644	633
-2	4	473	518	-6	8	465	471	7	1	437	425	0	5	462	488	13	0	303	339
-1	4	582	580	-5	8	867	843	10	1	632	631	2	5	575	568	14	0	449	455
0	4	566	530	-3	8	720	716	14	1	406	373	3	5	443	496	15	0	714	749
1	4	600	690	-2	8	257	269	16	1	341	330	4	5	368	373	17	0	288	286
2	4	622	667	0	8	291	230	17	1	319	277	5	5	761	782	-16	1	425	436
3	4	624	658	2	8	457	448	18	1	477	463	6	5	848	878	-15	1	333	354
4	4	289	307	3	8	1355	1304	-19	2	288	251	8	5	615	615	-12	1	539	554
5	4	687	681	4	8	286	319	-17	2	687	716	10	5	458	469	-11	1	402	417
6	4	691	706	6	8	361	391	-16	2	281	271								

TABLE 32: ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Nb	0.58136(2)	0.21418(5)	0.19528(4)	2.47*
As	0.20939(3)	0.15780(7)	0.26735(6)	3.31*
S1	0.52186(8)	0.1130(1)	0.0746(1)	3.26*
S2	0.57210(8)	0.3413(2)	0.0567(1)	3.60*
S3	0.51630(8)	0.1329(2)	0.31[illegible]9(1)	3.75*
S4	0.56193(8)	0.3659(1)	0.3010(1)	3.54*
S5	0.63390(8)	0.0503(1)	0.2242(1)	3.54*
S6	0.68163(7)	0.2798(2)	0.1989(1)	3.51*
C11	0.4876(3)	0.2027(6)	-0.0067(5)	2.82*
C12	0.4412(3)	0.1741(6)	-0.0731(5)	3.43*
C13	0.4164(3)	0.2420(7)	-0.1411(6)	4.21*
C14	0.4364(3)	0.3455(7)	-0.1445(6)	4.09*
C15	0.4824(3)	0.3765(6)	-0.0820(6)	3.69*
C16	0.5091(3)	0.3074(6)	-0.0132(5)	3.06*
C21	0.5210(3)	0.2120(7)	0.4254(5)	3.81*
C22	0.4989(4)	0.1770(7)	0.5182(7)	4.93*
C23	0.4971(4)	0.2458(9)	0.6005(7)	6.19*
C24	0.5165(4)	0.3452(9)	0.5921(7)	6.09*
C25	0.5395(3)	0.3818(7)	0.5039(7)	4.70*
C26	0.5405(3)	0.3143(6)	0.4180(6)	3.41*
C36	0.7256(3)	0.1716(6)	0.1733(5)	3.19*

Table 32 (continued)

ATOM	x	y	z	B
C35	0.7837(3)	0.1875(6)	0.1505(6)	3.86*
C34	0.8198(3)	0.1032(8)	0.1328(6)	4.97*
C33	0.7983(4)	0.0024(7)	0.1415(6)	5.04*
C32	0.7418(4)	-0.0137(6)	0.1648(6)	4.66*
C31	0.7040(3)	0.0717(6)	0.1835(5)	3.17*

RIGID BODIES

(a) Phenyl Carbon Atoms

C41	0.1589(2)	0.0435(3)	0.2397(4)	3.4(2)
C42	0.1656(3)	-0.0184(4)	0.1533(3)	4.1(2)
C43	0.1319(3)	-0.1087(4)	0.1387(4)	4.5(2)
C44	0.0915(2)	-0.1371(3)	0.2105(4)	4.7(2)
C45	0.0847(3)	-0.0752(4)	0.2968(3)	4.9(2)
C46	0.1184(3)	0.0151(4)	0.3114(4)	4.3(2)
D	3.710(3) [a]			
E	0.982(4)			
F	4.924(4)			
C51	0.1688(2)	0.2697(3)	0.3259(4)	3.4(2)
C52	0.1118(2)	0.2914(4)	0.2916(4)	4.4(2)
C53	0.0845(1)	0.3833(4)	0.3226(3)	4.9(2)
C54	0.1140(2)	0.4533(3)	0.3877(4)	4.9(2)
C55	0.1710(2)	0.4315(4)	0.4220(4)	4.7(2)
C56	0.1984(1)	0.3397(4)	0.3910(3)	4.0(2)

Table 32 (continued)

ATOM	x	y	z	B
D	5.779(3)			
E	2.731(4)			
F	4.418(3)			
C61	0.2679(4)	0.1098(4)	0.3600(10)	3.6(2)
C62	0.3211(5)	0.0725(4)	0.3265(5)	5.1(2)
C63	0.3613(3)	0.0279(4)	0.3961(7)	5.7(2)
C64	0.3482(4)	0.0207(4)	0.4990(10)	5.1(2)
C65	0.2950(5)	0.0580(4)	0.5318(5)	4.9(2)
C66	0.2548(3)	0.1026(4)	0.4622(7)	4.3(2)
D	2.023(3)			
E	1.217(8)			
F	5.084(8)			
C71	0.2370(5)	0.2098(4)	0.1429(8)	3.3(1)
C72	0.1963(5)	0.2212(4)	0.0622(4)	4.4(2)
C73	0.2126(7)	0.2680(5)	-0.0285(7)	5.5(2)
C74	0.2696(5)	0.3034(4)	-0.0384(8)	5.4(2)
C75	0.3103(5)	0.2920(4)	0.0423(4)	6.3(2)
C76	0.2940(7)	0.2452(5)	0.1330(7)	5.2(2)
D	1.109(4)			
E	2.521(8)			
F	4.425(8)			

Table 32 (continued)

ATOM	x	y	z	B
(b) Phenyl Hydrogen Atoms				
H1	0.7990	0.2619	0.1446	4.5
H2	0.8613	0.1152	0.1151	5.0
H3	0.8243	-0.0598	0.1281	5.0
H4	0.7250	-0.0880	0.1705	4.5
D	3.159			
E	0.277			
F	5.085			
H5	0.4840	0.1029	0.5229	5.4
H6	0.4809	0.2184	0.6663	6.0
H7	0.5158	0.3948	0.6530	6.0
H8	0.5537	0.4557	0.4962	5.4
D	3.448			
E	1.285			
F	1.748			
H9	0.4267	0.0982	-0.0685	4.1
H10	0.3826	0.2199	-0.1869	4.7
H11	0.4182	0.3963	-0.1949	4.7
H12	0.4978	0.4509	-0.0846	4.1
D	0.281			
E	2.406			
F	4.929			
H13	0.1945	0.0016	0.1020	4.6

Table 32 (continued)

ATOM	x	y	z	B
H14	0.1369	-0.1535	0.0773	5.1
H15	0.0674	-0.2020	0.2004	5.0
H16	0.0556	-0.0953	0.3482	5.5
H17	0.1132	0.0597	0.3730	5.1
D	3.707			
E	0.981			
F	5.973			
H18	0.0905	0.2414	0.2452	5.0
H19	0.0436	0.3989	0.2983	5.9
H20	0.0944	0.5191	0.4100	5.5
H21	0.1922	0.4816	0.4685	5.1
H22	0.2391	0.3241	0.4154	4.7
D	5.779			
E	2.732			
F	5.465			
H23	0.3305	0.0773	0.2529	5.1
H24	0.3994	0.0013	0.3725	6.1
H25	0.3770	-0.0107	0.5486	5.8
H26	0.2856	0.0531	0.6052	5.3
H27	0.2166	0.1290	0.4856	4.7
D	2.020			
E	1.219			
F	6.134			

Table 32 (continued)

ATOM	x	y	z	B
H28	0.1555	0.1957	0.0691	5.1
H29	0.1836	0.2756	-0.0864	5.6
H30	0.2814	0.3364	-0.1034	6.2
H31	0.3511	0.3173	0.0352	6.8
H32	0.3230	0.2374	0.1909	5.6
D	1.111			
E	2.515			
F	5.467			

*These values are equivalent isotropic temperature factors[81] corresponding to the anisotropic thermal parameters shown in Table 33.

[a] D, E, and F are the angles by which the coordinates of the rigid body are rotated with respect to a set of axes X, Y, Z. The origin of these axes is placed at the centre of the ring with the X axis parallel to a^*, the Z axis parallel to c, and the Y axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c.

TABLE 33: ANISOTROPIC THERMAL PARAMETERS ($\mathring{A}^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.0324(3)	0.0310(4)	0.0302(3)	-0.0003(3)	0.0007(2)	-0.0025(3)
As	0.0385(5)	0.0502(6)	0.0370(5)	-0.0037(4)	0.0025(4)	-0.0057(5)
S1	0.0510(12)	0.0340(11)	0.0383(11)	-0.0004(9)	-0.0071(9)	-0.0022(9)
S2	0.0515(12)	0.0430(12)	0.0420(11)	-0.0098(11)	-0.0024(9)	0.0051(10)
S3	0.0547(12)	0.0407(13)	0.0475(12)	-0.0054(10)	0.0120(10)	-0.0034(10)
S4	0.0413(11)	0.0397(12)	0.0535(12)	-0.0008(9)	0.0059(9)	-0.0093(10)
S5	0.0457(12)	0.0388(12)	0.0496(13)	0.0048(9)	-0.0042(10)	0.0083(10)
S6	0.0385(10)	0.0394(12)	0.0556(12)	-0.0022(10)	0.0009(9)	-0.0093(11)
C11	0.036(4)	0.036(5)	0.036(4)	-0.005(4)	-0.000(3)	-0.001(4)
C12	0.045(5)	0.048(5)	0.037(4)	-0.007(4)	-0.006(4)	0.000(4)
C13	0.049(5)	0.069(7)	0.041(5)	0.004(5)	-0.004(4)	0.004(5)
C14	0.054(5)	0.062(6)	0.039(5)	0.011(5)	-0.007(4)	0.008(5)
C15	0.053(5)	0.041(5)	0.046(5)	0.006(4)	0.002(4)	0.006(4)
C16	0.036(4)	0.049(5)	0.031(4)	0.006(4)	0.005(3)	-0.005(4)
C21	0.040(4)	0.066(6)	0.039(5)	0.006(5)	0.007(4)	-0.008(5)

Table 33 (continued)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C22	0.063(6)	0.067(7)	0.058(6)	0.008(5)	0.011(5)	0.010(5)
C23	0.079(7)	0.111(9)	0.045(6)	0.022(7)	0.011(5)	0.005(6)
C24	0.081(7)	0.109(9)	0.041(6)	0.032(7)	-0.006(5)	-0.021(6)
C25	0.045(5)	0.076(7)	0.057(6)	0.014(5)	-0.011(4)	-0.025(5)
C26	0.040(4)	0.044(5)	0.046(5)	0.006(4)	0.000(4)	-0.007(4)
C31	0.038(4)	0.048(5)	0.034(4)	0.010(4)	-0.002(4)	0.001(4)
C32	0.061(6)	0.053(6)	0.063(6)	0.010(5)	-0.004(5)	0.011(5)
C33	0.061(6)	0.067(7)	0.064(6)	0.029(5)	0.010(5)	0.012(5)
C34	0.043(5)	0.086(7)	0.061(6)	0.020(5)	0.005(4)	0.019(6)
C35	0.040(5)	0.066(6)	0.040(5)	0.003(4)	-0.004(4)	0.007(4)
C36	0.045(5)	0.042(5)	0.034(4)	0.007(4)	-0.002(4)	0.002(4)

TABLE 34: INTRA-IONIC CONTACTS (Å)

ATOMS	DISTANCE	ATOMS	DISTANCE
Nb-S1	2.428(2)	S2-S6	3.178(3)
Nb-S2	2.442(2)	S4-S6	3.294(3)
Nb-S3	2.458(2)	S1-C11	1.736(7)
Nb-S4	2.433(2)	S2-C16	1.740(7)
Nb-S5	2.436(2)	S3-C21	1.747(7)
Nb-S6	2.451(2)	S4-C26	1.760(8)
As-C41	1.891(4)	S5-C31	1.739(7)
As-C51	1.883(4)	S6-C36	1.750(7)
As-C61	1.880(4)	C11-C12	1.402(9)
As-C71	1.896(4)	C12-C13	1.356(10)
S1-S2	3.143(3)	C13-C14	1.398(10)
S3-S4	3.160(3)	C14-C15	1.374(10)
S5-S6	3.147(3)	C15-C16	1.392(9)
S1-S3	3.204(3)	C16-C11	1.424(9)
S1-S5	3.282(3)	C21-C22	1.410(10)
S3-S5	3.184(3)	C22-C23	1.396(12)
S2-S4	3.245(3)	C23-C24	1.349(13)
C24-C25	1.374(12)	C33-C34	1.383(12)
C25-C26	1.422(10)	C34-C35	1.382(11)
C26-C21	1.385(10)	C35-C36	1.395(9)
C31-C32	1.419(10)	C36-C31	1.375(10)
C32-C33	1.36[illegible](11)		

TABLE 35: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Nb-S2	80.40(7)	Nb-S3-C21	105.5(3)
S3-Nb-S4	80.47(7)	Nb-S4-C26	105.4(3)
S5-Nb-S6	80.18(7)	Nb-S5-C31	106.1(3)
S1-Nb-S5	84.87(7)	Nb-S6-C36	106.0(3)
S1-Nb-S3	81.94(7)	S1-C11-C16	120.2(6)
S3-Nb-S5	81.18(7)	S2-C16-C11	119.0(5)
S2-Nb-S4	83.46(7)	S3-C21-C26	119.7(6)
S2-Nb-S6	81.03(7)	S4-C26-C21	121.1(6)
S4-Nb-S6	84.81(7)	S5-C31-C36	121.1(6)
S1-Nb-S4	133.25(7)	S6-C36-C31	119.9(6)
S1-Nb-S6	134.51(7)	C41-As-C51	110.6(2)
S3-Nb-S2	136.61(7)	C41-As-C61	107.1(2)
S3-Nb-S6	136.50(7)	C41-As-C71	109.0(2)
S5-Nb-S2	135.63(7)	C51-As-C61	109.6(2)
S5-Nb-S4	133.86(7)	C51-As-C71	105.9(2)
Nb-S1-C11	106.5(2)	C61-As-C71	114.6(2)
Nb-S2-C16	106.1(3)	C11-C12-C13	122.4(7)
C12-C13-C14	119.5(7)	C25-C26-C21	120.0(8)
C13-C14-C15	120.0(7)	C26-C21-C22	119.1(8)
C14-C15-C16	121.2(7)	C31-C32-C33	121.1(8)
C15-C16-C11	120.0(7)	C32-C33-C34	120.3(8)
C16-C11-C12	117.8(6)	C33-C34-C35	119.5(8)

Table 35 (continued)

ATOMS	ANGLES	ATOMS	ANGLES
C21-C22-C23	119.6(8)	C34-C35-C36	120.4(8)
C22-C23-C24	120.5(9)	C35-C36-C31	120.5(7)
C23-C24-C25	121.8(10)	C36-C31-C32	118.0(7)
C24-C25-C26	119.9(9)	S3-S1-S5	58.80(6)
S6-S2-S4	61.69(6)	S5-S3-S1	61.83(6)
S2-S4-S6	58.16(6)	S3-S5-S1	59.37(6)
S2-S6-S4	60.15(6)		

TABLE 36: INTER-IONIC CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H9	$\bar{x}+1$, $\bar{y}$, $\bar{z}$	2.942
S1	H20	1/2-x, 1/2+y-1, 1/2-z	2.942
S1	C54	1/2+x, 1/2-y, 1/2+z-1	3.409(6)
S1	S1	$\bar{x}+1$, $\bar{y}$, $\bar{z}$	3.607(4)
S1	C53	1/2+x, 1/2-y, 1/2+z-1	3.661(6)
S2	H17	1/2+x, 1/2-y, 1/2+z-1	2.913
S3	H15	1/2-x, 1/2+y, 1/2-z	2.855
S4	H3	1/2-x+1, 1/2+y, 1/2-z	2.901
S4	C44	1/2-x, 1/2+y, 1/2-z	3.523(5)
S4	C45	1/2-x, 1/2+y, 1/2-z	3.640(5)
S5	H25	$\bar{x}+1$, y, $\bar{z}+1$	3.048
S6	H29	1/2+x, 1/2-y, 1/2+z	2.908
S6	C33	1/2-x+1, 1/2+y, 1/2-z	3.549(9)
S6	C32	1/2-x+1, 1/2+y, 1/2-z	3.606(8)
S6	C73	1/2+x, 1/2-y, 1/2+z	3.680(5)
C35	C65	1/2+x, 1/2-y, 1/2+z-1	3.612(10)
C35	C66	1/2+x, 1/2-y, 1/2+z-1	3.688(9)
C34	H14	$\bar{x}+1$, $\bar{y}$, $\bar{z}$	3.038
C32	H21	1/2+x, 1/2-y, 1/2+z-1	2.811
C32	C55	1/2+x, 1/2-y, 1/2+z-1	3.682(9)
C31	H21	1/2+x, 1/2-y, 1/2+z-1	2.909
C31	C55	1/2+x, 1/2-y, 1/2+z-1	3.495(8)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C21	C44	1/2-x, 1/2+y, 1/2-z	3.638(9)
C23	H18	1/2+x, 1/2-y, 1/2+z	2.821
C23	C52	1/2+x, 1/2-y, 1/2+z	3.606(11)
C25	H28	1/2+x, 1/2-y, 1/2+z	2.942
C25	H8	$\bar{x}+1, \bar{y}+1, \bar{z}+1$	2.980
C25	C25	$\bar{x}+1, \bar{y}+1, \bar{z}+1$	3.517(17)
C26	H15	1/2-x, 1/2+y, 1/2-z	2.886
C26	C44	1/2-x, 1/2+y, 1/2-z	3.472(8)
C11	C53	1/2+x, 1/2-y, 1/2+z-1	3.400(9)
C12	H20	1/2-x, 1/2+y-1, 1/2-z	3.049
C12	C53	1/2+x, 1/2-y, 1/2+z-1	3.685(9)
C13	H6	x, y, z-1	2.996
C13	C75	x, y, z	3.549(10)
C13	H31	x, y, z	2.966
C16	H16	1/2-x, 1/2+y, 1/2-z	2.947
C42	C56	1/2-x, 1/2+y-1, 1/2-z	3.676(7)
C44	H32	1/2-x, 1/2+y-1, 1/2-z	2.811
C44	C76	1/2-x, 1/2+y-1, 1/2-z	3.609(7)
C45	H31	1/2-x, 1/2+y-1, 1/2-z	2.947
C45	H12	1/2+x-1, 1/2-y, 1/2+z	3.023
C45	C75	1/2-x, 1/2+y-1, 1/2-z	3.577(8)
C45	C76	1/2-x, 1/2+y-1, 1/2-z	3.699(7)
C53	C63	1/2-x, 1/2+y, 1/2-z	3.672(7)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C54	H23	1/2-x, 1/2+y, 1/2-z	2.778
C54	C62	1/2-x, 1/2+y, 1/2-z	3.574(7)
C55	H23	1/2-x, 1/2+y, 1/2-z	2.956
C64	C73	1/2-x, 1/2+y-1, 1/2-z	3.537(8)
C65	H1	1/2+x-1, 1/2-y, 1/2+z	2.731
C65	C74	1/2-x, 1/2+y-1, 1/2-z	3.571(8)
C66	H1	1/2+x-1, 1/2-y, 1/2+z	3.095
H9	H20	1/2-x, 1/2+y-1, 1/2-z	2.380

TABLE 37: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Nb, S1, S2

EQUATION OF PLANE: $-0.8413X + 0.3686Y + 0.3953Z + 9.1444 = 0.0$ [a]

(B) ATOMS FORMING PLANE: Nb, S3, S4

EQUATION OF PLANE: $0.7683X - 0.2315Y + 0.5967Z - 11.0967 = 0.0$

(C) ATOMS FORMING PLANE: Nb, S5, S6

EQUATION OF PLANE: $-0.0706X + 0.1393Y + 0.9877Z - 1.9792 = 0.0$

(D) ATOMS FORMING PLANE: S1, S2, C11, C12, C13, C14 C15, C16

EQUATION OF PLANE: $-0.6239X + 0.3044Y + 0.7198Z + 6.3172 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S1	-0.001(2)	S2	0.009(2)
C11	-0.048(7)	C12	0.041(7)
C13	0.078(8)	C14	0.010(8)
C15	-0.071(8)	C16	-0.086(7)
Nb	-0.7144(6)		

(E) ATOMS FORMING PLANE: S3, S4, C21, C22, C23, C24, C25, C26

Table 37 (continued)

EQUATION OF PLANE: 0.9191X - 0.3096Y + 0.2438Z - 11.2653 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

S3	0.004(2)	S4	0.004(2)
C21	-0.090(7)	C22	-0.012(9)
C23	-0.067(9)	C24	0.060(9)
C25	-0.023(8)	C26	-0.067(7)
Nb	-0.7099(6)		

(F) ATOMS FORMING PLANE: S5, S6, C31, C32, C33, C34, C35, C36.

EQUATION OF PLANE: 0.2788X + 0.0011Y + 0.9603Z - 6.8577 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

S5	-0.006(2)	S6	0.001(2)
C31	0.036(7)	C32	-0.042(8)
C33	-0.052(9)	C34	-0.004(9)
C35	0.057(8)	C36	0.055(7)
Nb	0.6869(6)		

(G) ATOMS FORMING PLANE: S1, S3, S5

EQUATION OF PLANE: -0.3396X - 0.9393Y + 0.0484Z + 5.3688 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

Nb	1.5787(6)

(H) ATOMS FORMING PLANE: S2, S4, S6

Table 37 (continued)

EQUATION OF PLANE: $-0.3423X - 0.9380Y + 0.0545Z + 8.5348 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

Nb	-1.5699(6)

[a]X, Y and Z are in Å and refer to the orthogonal coordinates along *a*, *b*, *c**.

TABLE 38: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
Nb, S1, S2	Nb, S3, S4	119.7°
Nb, S1, S2	Nb, S5, S6	120.1°
Nb, S3, S4	Nb, S5, S6	120.2°
Nb, S1, S2	S1, S2, C11, C12, C13, C14, C15, C16	22.8°
Nb, S3, S4	S3, S4, C21, C22, C23, C24, C25, C26	22.6°
Nb, S5, S6	S5, S6, C31, C32, C33, C34, C35, C36	21.8°
S1, S3, S5	S2, S4, S6	0.6°

DESCRIPTION OF STRUCTURE

The portion of the molecule of major interest, i.e. the $Nb(bdt)_3^-$ anion, is shown in the three dimensional representation in Fig. 14. The metal is surrounded approximately equidistantly by six sulfur atoms in the form of a trigonal prism, thus it has approximate C_{3h} symmetry. The dithiolene ligands radiate from the metal in a "paddle-wheel" arrangement as was the case for $Mo(bdt)_3$ and the other trigonal prismatic dithiolenes.[129,130,132] The prism is not however as regular as that in $Mo(bdt)_3$, with a significant range in niobium-sulfur distances from 2.428(2) Å to 2.458(2) Å. The mean Nb-S distance (2.441 Å) is also significantly longer than the Mo-S distance (2.367 Å) in $Mo(bdt)_3$ and thus is the longest metal-sulfur distance observed in any of the trigonal prismatic molecules (Table 48).

It is interesting that in the previous trigonal prismatic structures the metal-sulfur bond lengths had been amazingly constant, considering that the covalent and ionic radii[133] of vanadium differed, by approximately 0.07 Å, from those of molybdenum and rhenium. $Nb(bdt)_3^-$ is therefore the first example of a prism in which this is no longer true; the Nb-S distance being approximately 0.11 Å longer than

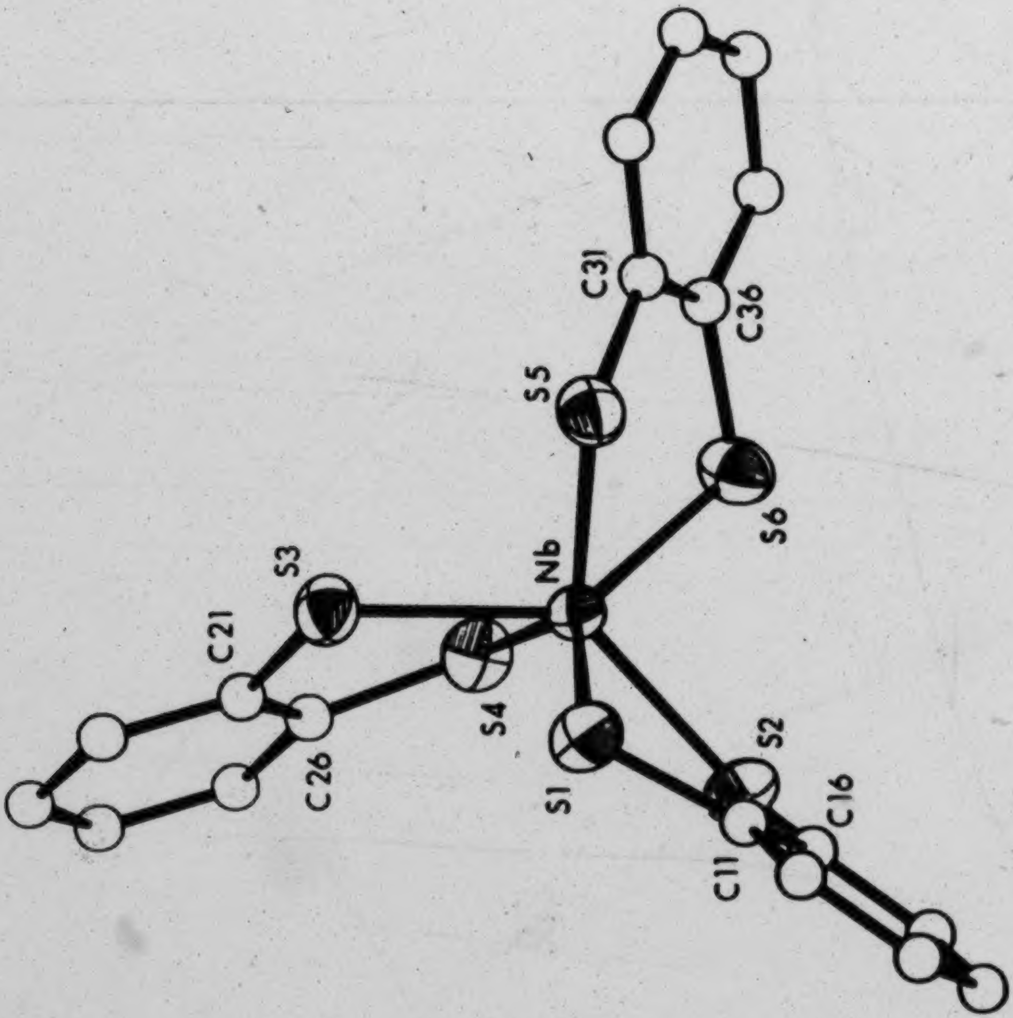

S5
C31
C36
S6
Nb
S3
C21
S4
C26
S1
S2
C16
C11

Fig. 14: A PERSPECTIVE VIEW OF THE $Nb(S_2C_6H_4)_3^-$ ANION.

the metal-sulfur distances in the three other prisms and also 0.074 Å longer than in Mo(bdt)$_3$ (to which this comparison is most useful). The increase in metal-sulfur distances progressing from the molybdenum to the niobium complex is approximately consistent with the corresponding increase in the metal covalent radii.[133] Although the values for the metal covalent radii are ambiguous (especially for Nb(bdt)$_3^-$ since the extra electron will expand the niobium orbitals increasing its radius from that of the neutral species), a very rough comparison is obtained using Pauling's values. This yields a predicted increase in metal-sulfur bonds of about 0.05 Å when calculated using the neutral atom radii.

The constancies of the metal-sulfur distances in the previous trigonal prisms, in spite of differing metal radii, had been attributed as a consequence of proposed interligand S-S bonding.[124] Thus the difference in Nb-S distances compared with Mo-S distances tends to indicate a possible breakdown in S-S bonding and an expected increase in S-S distances. Because of the relatively fixed ligand bite this should manifest itself in longer interligand S-S distances compared to intraligand S-S distances. This is in fact what is observed with the mean interligand S-S distance (3.231 Å) being significantly longer than the intraligand S-S distance (3.150 Å). Here again slight distortions are obvious with a range in interligand S-S distances from 3.178(3) Å to 3.294(3) Å.

The sulfur-carbon distances (1.745 Å), although similar to the other *tris* dithiolenes, are longer than any observed previously and more significantly are longer than those in Mo(bdt)$_3$ (1.727 Å) where the same ligand is involved. Thus the sulfur-carbon bonds have less double bond character in the niobium complex and the ligands are therefore more dithiolate and less dithioketonic in character than for Mo(bdt)$_3$. The mean carbon-carbon distance within the ligands is again consistent with those observed in benzene[158] and in several disubstituted benzene derivatives,[159] as mentioned in Chapter VI. Again, as was the case for Mo(bdt)$_3$, there is a wide range in C-C distances (Fig. 15). From the diagram showing the average C-C bond lengths one sees that the C2-C3, C3-C4, and C4-C5 distances are significantly shorter than the other three. This may be interpreted as indicating some contribution from the dithioketonic formulation but this simple interpretation should not be made in the absence of a full analysis of the thermal

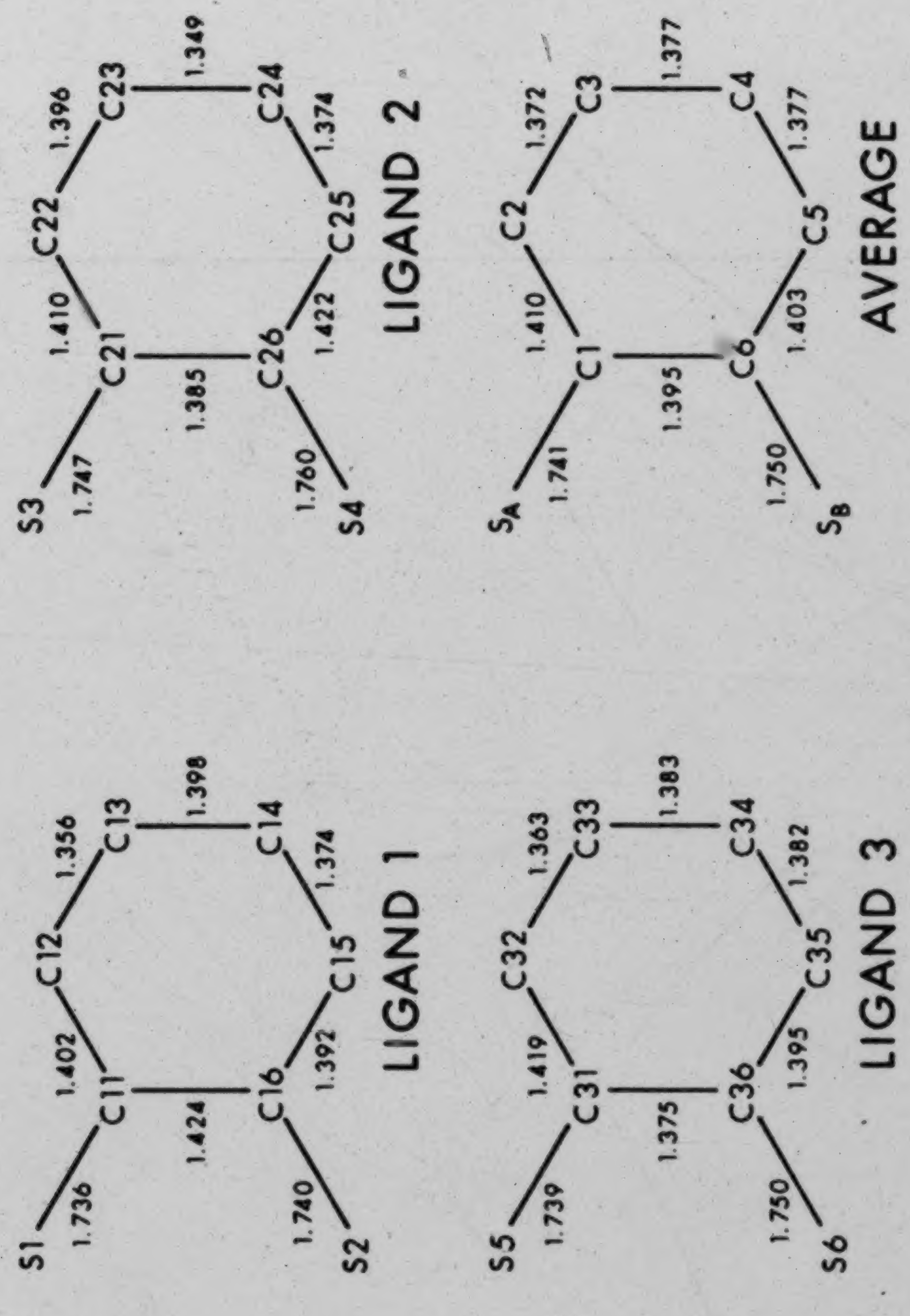

LIGAND 2
S3
C21
C22
C23
C24
C25
C26
S4
1.747
1.410
1.396
1.349
1.374
1.422
1.385
1.760
AVERAGE
S_A
C1
C2
C3
C4
C5
C6
S_B
1.741
1.410
1.372
1.377
1.377
1.403
1.395
1.750
LIGAND 1
S1
C11
C12
C13
C14
C15
C16
S2
1.736
1.402
1.356
1.398
1.374
1.392
1.424
1.740
LIGAND 3
S5
C31
C32
C33
C34
C35
C36
S6
1.739
1.419
1.363
1.383
1.382
1.395
1.375
1.750

Fig. 15: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.

parameters and an assessment of their effect on the observed uncorrected bond distances.

The intra- and interligand S-Nb-S angles average 80.35° and 82.88° respectively and are therefore an indication of the slight distortion from trigonal prismatic coordination. Possibly a more significant indication of the distortion, however, is the *range* in the interligand S-Nb-S angles, from 84.87(7)° to 81.03(7)°. The S-Nb-S angles, involving sulfur atoms approximately *trans* to each other, average 135.06° and is again similar to the value of 136(1)° found in the other prisms.

The two triangular faces of the prism deviate slightly from being parallel, the angle between their normals being 0.6°. In addition the angles between the NbS_2 planes, as shown in Table 38, are all close to the expected 120°. The Nb-S-C angles average 105.9° and are all in close agreement with each other.

The S-C-C angles (S_A-C_1-C_6 and S_B-C_6-C_1 in Fig. 15) average 120.1° and are close to the expected value of 120°. This good internal agreement of the Nb-S-C and S-C-C angles adds further proof that the deviations in the interligand S-Nb-S angles are indeed significant.

As was observed in $Mo(bdt)_3$, $Mo(S_2C_2H_2)_3$,[130] and $Mo[Se_2C_2(CF_3)_2]_3$,[152] the ligand planes again deviate considerably from the corresponding MS_2 planes. These deviations are more regular in $Nb(bdt)_3^-$ than in $Mo(bdt)_3$ (see Table 49). Their mean values, 22.4° and 21.4°, respectively are however in good agreement and both are larger than the values of 18° and 18.6° observed in $Mo(S_2C_2H_2)_3$ and $Mo[Se_2C_2(CF_3)_2]_3$ respectively. That these dihedral angles are irregular in $Mo(bdt)_3$ yet regular in $Nb(bdt)_3^-$ is probably a consequence of packing forces. The flexibility, afforded by the rotational freedom of the phenyl groups of the tetraphenylarsonium cation, allows effective packing without major deformation of the ligand planes. It is probable then that the structure, observed in the crystal, closely approximates the structure in solution. It is interesting that this bend of the ligand plane from the MS_2 plane has been observed in the trigonal prismatic molybdenum dithiolenes and also in the molybdenum diselenato complex, and now has been observed in $Nb(bdt)_3^-$, which is isoelectronic with the molybdenum analogue. In contrast, the ligand planes were found to be coplanar with the MS_2 planes in both $Re(S_2C_2Ph_2)_3$[129] and $V(S_2C_2Ph_2)_3$.[132]

A three dimensional representation of the

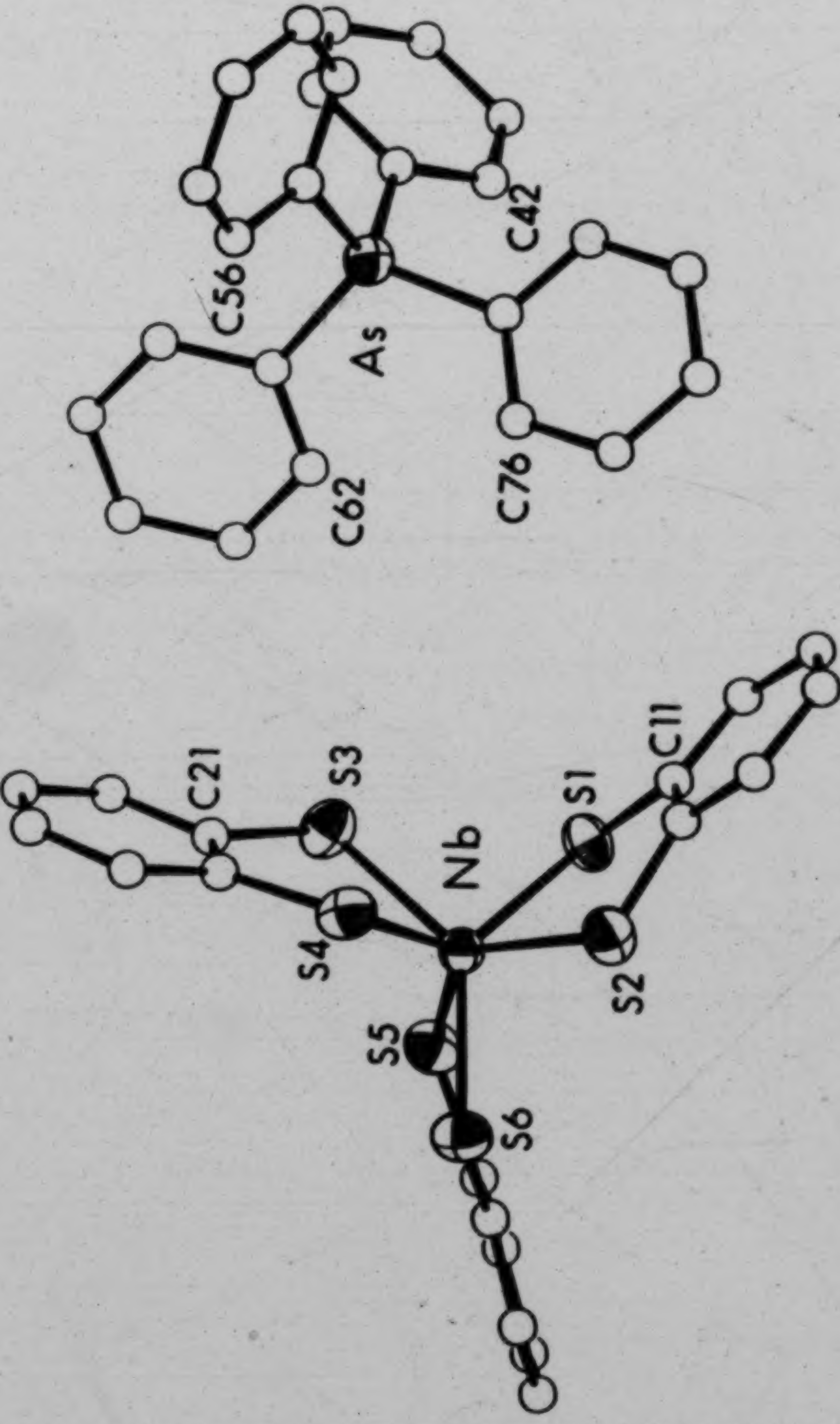

C56
C42
As
C62
C76
C21
S3
C11
S1
Nb
S4
S2
S5
S6

Fig. 16: A PERSPECTIVE VIEW OF $[As(C_6H_5)_4][Nb(S_2C_6H_4)_3]$, VIEWED DOWN THE CRYSTALLOGRAPHIC *b* AXIS.

$Nb(bdt)_3^-$ anion and the tetraphenylarsonium cation, viewed down the crystallographic *b* axis, is shown in Fig. 16. The geometry of the cation is quite normal with no unusual features. The arsenic atom is surrounded in almost perfect tetrahedral coordination with the C-As-C angles being close to the predicted 109.5°, and all deviations from this value are easily explained by intermolecular interactions. The arsenic-carbon bonds are similar and the mean (1.888 Å) approximates the value predicted from the sums of the covalent radii[133,162] (1.94 Å), assuming an arsenic-carbon single bond involving sp^2 hybridized carbon atoms. These observed bond lengths agree favourably with other determinations[163,164] where the tetraphenylarsonium cation was involved.

CHAPTER VIII: THE CRYSTAL AND MOLECULAR STRUCTURE OF *BIS* (TETRAMETHYLAMMONIUM) *TRIS* (BENZENE-1,2-DITHIOLATO) ZIRCONIUM, ($[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$).

EXPERIMENTAL

Bright red crystals of $[(CH_3)_4N]_2[Zr(bdt)_3]$, suitable for single crystal X-ray diffraction studies, were kindly supplied by Dr. Takats and Mr. Martin. These crystals were prepared[143] by the reaction of sodium cyclopentadienide and benzene dithiol and the subsequent reaction with $Zr[N(C_2H_5)_2]_4$, and crystallization with tetramethylammonium chloride. Preliminary photography showed mmm Laué symmetry indicating an orthorhombic space group. Systematic absences determined by Weissenberg ($0k\ell$, $1k\ell$; CuK_α X-radiation) and Precession photography ($h0\ell$, $h1\ell$, $hk0$, $hk1$; MoK_α X-radiation) are $h00$: $h = 2n + 1$, and $0k0$: $k = 2n + 1$ consistent with the space group $P2_12_12$. Precise lattice parameters were obtained at 22° from a least squares analysis performed on the setting angles of 12 high angle reflections, accurately centred on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation. The resulting cell parameters and estimated standard deviations are: $a = 9.931(2)$ Å, $b = 14.368(2)$ Å, $c = 11.098(2)$ Å The observed density [1.38(2) g cm^{-3}], obtained by floatation in a mixture of chloro- and bromobenzene is consistent with the theoretical value of 1.381 g cm^{-3}, calculated assuming two molecules with formula weight 660.19 a.m.u. occupy the unit cell of volume 1587.9 Å^3. Since the space group $P2_12_12$ has four general equivalent positions, the $Zr(bdt)_3^{2-}$ dianion is therefore restricted to having 2-fold symmetry and must sit on the crystallographic 2-fold axis. The two tetramethylammonium cations can either be related by the two-fold or sit on the two-fold axis.

Intensity data were collected on the Picker automatic diffractometer using CuK$_\alpha$ X-radiation filtered with a 0.0005" thick nickel foil and using a 2° take-off angle. The crystal was mounted in a general orientation but with the a^* axis approximately coincident with the ϕ axis of the diffractometer. A coupled $2\theta/\omega$ scan technique, with a scan speed of 1° min^{-1}, was employed for data collection with all unique reflections with $2\theta \leq 125°$ being collected. The two theta scan range for each reflection was $2° + \Delta 2\theta$ where $\Delta 2\theta$ corresponded to $[2\theta(K_{\alpha_1}) - 2\theta(K_{\alpha_2})]$.

Forty second stationary background counts on each side of the peak were recorded and assuming linearity of background, intensities and standard deviations in the intensities were calculated as shown in Chapter II using a "p factor" of 0.03. A scintillation counter was used in conjunction with a pulse height analyzer, tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition several additional reflections were collected manually to assess decomposition. No significant decomposition was observed so no correction was necessary.

Of the 1403 unique reflections collected, 1054 were significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The significant data were then reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. Standard deviations in the structure factors were again calculated as in Chapter II.

The crystal faces were identified and their perpendicular distances to an arbitrarily chosen origin measured as: $(0,1,0)$, 3.268×10^{-3} cm; $(0,\bar{1},0)$, 10.836×10^{-3} cm; $(\bar{1},0,0)$, 20.640×10^{-3} cm; $(0,0,1)$, 3.09×10^{-3} cm; $(1,1,0)$, 0.0 cm; $(1,\bar{1},0)$, 0.0 cm; and $(1,0,\overline{12})$, 0.0 cm. The face $(1,0,\overline{12})$ is acknowledged as a very unusual choice, but its position is most consistent with the indices chosen, since it is opposite to the (0,0,1) face but inclined to it by about 5°. The absorption coefficient[86] for CuK_α X-radiation is 66.63 cm^{-1}, leading to a range in transmission factors from 0.756 to 0.423.

In the original data collection several irregularities were observed. These occurred as "pulses" in the counter and their exact cause was unknown, but was probably due to some electronic device connected to the diffractometer power line. The reflections where this was actually observed were rejected. However it was believed (on the basis that several $|F_o|$ values were extremely high) that these pulses had occurred throughout the data collection. For this reason the $hk\ell$ data were recollected along with the $h\overline{k\ell}$ data so all three data sets could be compared and faulty reflections could be excluded. The second $hk\ell$ data set was merged with the $h\overline{k\ell}$ data to obtain improved standard deviations. In this merged data set the number of statistically reliable reflections increased to 1126. The same data collection techniques were used for the second $hk\ell$ data and the $h\overline{k\ell}$ data as was used for the original $hk\ell$ data. Terms used in the Zachariasen extinction correction were calculated at this stage.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened Patterson map[146] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. Since the zirconium atom is restricted to lie on the two-fold axis, the Harker vectors are located at 1/2, 1/2, 2z; and 1/2, 1/2, -2z, so the solution is trivial yielding the coordinates for the zirconium as (0.0, 0.0, 0.189) from the largest vector at (0.5, 0.5, 0.378). The next six most intense vectors could be interpreted as Zr-S vectors about either the origin or the Zr-Zr Harker vector. From initial inspection of the placement of these vectors, it was evident that the zirconium coordination was close to octahedral and was definitely not trigonal prismatic. Due to the extra symmetry of the Patterson, care had to be taken in choosing the vectors to represent the three independent sulfur atoms, in order for the model to phase correctly. Several arbitrary choices can be made initially. The S1 position was calculated from the vector at (0.05, 0.168, 0.0) yielding the coordinates (0.05, 0.168, 0.189). From the vector at (0.16, 0.0, 0.18) the S2 position was calculated as (0.16, 0.0, 0.009). The position of S3, however, must be chosen in such a way to be consistent with the choice of S1 and S2. There are two possible choices for the S3 position yielding the positions (0.185, -0.048, 0.315) or (0.185, 0.048, 0.315). A choice between the two was made on the basis of sulfur-sulfur vectors which showed the first position was correct.

In the first refinements, involving only the zirconium and sulfur positions, the y coordinate of S2 was not refined, since it was possible that it could refine in the wrong direction and hamper the phasing. A brief resumé of the refinement is shown in Table 39.

TABLE 39: REFINEMENT OUTLINE

	MODEL	R_1	R_2
(1)	Zr and S atoms	0.297	0.384
(2)	Complete anion (isotropic B's)	0.152	0.243
(3)	Anion and Cation (isotropic B's)	0.088	0.106
(4)	Anisotropic Zr and S	0.074	0.097
(5)	Anisotropic Zr, S, N and C atoms of tetramethyl ammonium	0.069	0.088
(6)	Absorption Correction	0.050	0.063
(7)	Change of Hand	0.057	0.073
(8)	Carbon atoms of dithiolene ligands anisotropic	0.042	0.061
(9)	Hydrogen atoms of dithiolene ligands	0.039	0.059
(10)	Extinction correction[147]	0.039	0.059
(11)	Merged Data	0.034	0.053
(12)	Methyl Hydrogens included as rotors	0.029	0.035

Structure factors were calculated using the atomic scattering factors for the neutral atoms for zirconium, sulfur, carbon and nitrogen by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] Anomalous dispersion corrections by Cromer[76] were applied to the zirconium and sulfur scattering factors ($\Delta f'_{Zr} = -0.62$, $\Delta f''_{Zr} = 2.42$, $\Delta f'_{S} = 0.31$, $\Delta f''_{S} = 0.58$).

A refinement was performed with a change of hand for model (6) and the original model was judged significantly better on the basis of a Hamilton's R test[79] (at the 0.005 significance level). Hydrogen positions on the dithiolene ligands were calculated from the known geometry and orientation of the benzene rings, using a C-H distance of 1.0 Å. The hydrogen parameters were not refined. The hydrogen atoms were given thermal parameters approximately 10 - 15% greater than their attached carbon atom. An electron density difference map, phased on model (11), failed to locate any of the methyl hydrogen atoms, instead only smears of electron density were observed in the predicted regions. In addition the tetramethylammonium carbon atoms had anomalous thermal parameters, so the difference map was inspected for obvious signs of disorder involving these carbon atoms. No signs of disorder, however, were obvious. Although the methyl hydrogens were not located, they were added to the structure factor calculations in the form of free rotating rigid bodies.[165] The ideal tetrahedral coordination of the carbon atoms was assumed and the centres of gravity and angles defining the orientation of the "hydrogen triangles" were calculated using the assumed geometry, and the direction cosines of the nitrogen-carbon bonds.

Model (11), which is the refinement of the merged data, contains all the corrections performed on the previous models.

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 40. The final fractional coordinates and isotropic temperature factors of all atoms are shown in Table 41. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 42 shows the anisotropic thermal parameters (U_{ij}'s)[80] of all anisotropic atoms. Relevant bond lengths and angles are shown in Tables 43 and 44, and were obtained with their standard deviations from ORFFE. Several interionic contacts which are comparable to the predicted van der Waals contacts[151] are shown in Table 45. Selected least squares planes are shown in Table 46. In addition Table 47 lists the dihedral angles between selected planes.

The numbering scheme for all non-hydrogen atoms is shown in Figures 17 and 18. The hydrogen atoms H1 through H6 are attached sequentially to the carbon atoms (C2 through C9) which are not bonded to sulfur atoms. The hydrogen atoms H7 through H18 are bonded sequentially in groups of three to carbon atoms C10 through C13. Since the hydrogen atoms of the methyl groups were included as hindered rotors, no individual temperature factors are given, rather the temperature factors for the groups are shown in Table 41.

TABLE 40: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL
***H =	0****		
0	1	807	853
0	2	797	721
0	3	114	111
0	4	217	214
0	5	784	806
0	6	967	1008
0	7	402	407
0	8	106	167
0	9	554	545
0	10	190	189
0	11	117	106
1	1	1146	1164
1	2	345	319
1	3	400	402
1	4	216	225
1	5	167	167
1	6	718	727
1	7	712	709
1	9	201	214
1	11	178	184
1	12	240	239
2	0	420	427
2	1	724	686
2	2	296	311
2	3	658	671
2	4	266	279
2	5	680	657
2	6	589	582
2	8	217	211
2	9	188	181
2	10	223	209
2	11	223	222
2	12	158	143
3	1	376	377
3	2	184	111
3	3	221	233
3	5	235	253
3	6	214	218
3	7	662	675
3	8	214	210
3	9	221	213
3	10	174	169
3	12	308	309
4	0	1678	1630
4	1	754	734
4	2	213	208
4	3	178	188
4	4	131	126
4	5	283	262
4	6	734	736
4	8	160	157
4	9	142	147
4	10	186	199
4	11	159	170
4	12	79	83
5	1	860	890
5	2	426	432
5	3	177	185
5	4	587	576
5	6	381	386
5	7	487	485
5	8	88	67
5	9	263	255
5	11	216	218
6	0	1678	1703
6	1	373	380
6	2	343	351
6	3	286	278
6	4	470	430
6	5	865	866
6	6	298	305
6	7	244	241
6	9	202	192
6	10	269	266
6	11	166	171

K	L	FOBS	FCAL
7	1	148	148
7	2	495	493
7	3	312	307
7	4	427	429
7	5	177	167
7	6	569	570
7	7	216	216
7	8	135	144
7	9	137	148
7	10	167	185
7	11	214	230
8	0	388	381
8	1	632	642
8	3	206	204
8	4	197	198
8	5	419	417
8	6	147	132
8	7	191	179
8	10	202	202
9	1	186	187
9	2	285	291
9	4	258	256
9	7	317	304
9	8	231	262
9	9	144	138
9	10	144	155
10	0	414	397
10	1	337	331
10	3	347	348
10	4	151	128
10	5	305	300
10	6	214	213
11	1	156	143
11	2	357	405
11	3	168	156
11	4	478	469
11	5	144	141
11	6	281	288
11	7	94	112
11	8	96	98
11	9	147	167
12	0	395	390
12	1	279	295
12	2	163	164
12	3	287	281
12	4	159	160
12	5	397	393
12	7	85	95
13	1	186	187
13	2	128	124
13	3	97	107
13	4	183	173
13	6	192	206
13	7	121	121
14	0	180	184
14	1	128	122
14	3	112	101
14	5	90	113
14	6	84	103
15	2	132	118
15	4	96	91
16	0	181	179
16	1	93	108
***H =	1****		
0	1	682	709
0	2	659	672
0	3	514	534
0	4	623	610
0	5	115	96
0	6	808	794
0	7	843	829
0	8	262	281
0	9	397	404
0	11	192	190
0	12	206	208
1	0	1585	1547

K	L	FOBS	FCAL
1	1	538	514
1	2	962	955
1	3	533	537
1	5	635	628
1	6	566	562
1	7	343	338
1	8	264	254
1	9	205	204
1	10	265	262
1	11	164	168
2	1	314	265
2	2	939	936
2	3	399	400
2	4	581	595
2	5	246	259
2	6	265	261
2	7	408	417
2	8	222	228
2	9	192	197
2	10	213	203
2	11	106	98
2	12	234	224
3	0	1665	1617
3	1	542	532
3	2	240	242
3	4	278	261
3	5	330	325
3	6	823	826
3	7	145	143
3	8	173	150
3	10	83	99
3	11	240	249
3	12	98	88
4	0	338	319
4	1	271	280
4	2	307	292
4	3	387	403
4	4	210	198
4	5	151	149
4	6	445	440
4	7	521	517
4	8	154	141
4	9	279	279
4	10	151	156
4	11	130	150
4	12	209	218
5	0	1388	1371
5	1	613	615
5	2	580	561
5	3	379	370
5	4	383	378
5	5	692	692
5	6	299	310
5	7	263	255
5	8	320	333
5	9	135	150
5	10	311	303
5	11	162	160
6	0	293	287
6	1	743	725
6	2	478	487
6	3	351	335
6	4	738	740
6	5	163	160
6	6	567	581
6	7	322	339
6	8	192	198
6	9	282	288
6	10	184	149
6	11	182	196
7	0	671	677
7	1	443	435
7	2	432	441
7	3	903	903
7	4	171	173
7	5	506	498

K	L	FOBS	FCAL
7	6	262	256
7	7	151	150
7	8	159	160
7	10	183	195
7	11	158	165
8	1	167	164
8	2	306	309
8	3	152	157
8	4	378	381
8	5	151	148
8	6	141	136
8	7	261	261
8	8	193	209
8	9	206	214
8	10	163	166
9	0	343	344
9	1	207	214
9	3	107	114
9	5	143	153
9	6	248	245
9	8	141	154
9	10	114	124
10	1	137	135
10	2	224	223
10	3	167	160
10	4	233	222
10	6	243	227
10	7	218	215
10	8	108	112
10	9	149	155
11	0	441	444
11	1	265	262
11	2	205	202
11	3	335	338
11	4	177	173
11	5	409	396
11	7	111	100
11	8	119	122
12	0	143	160
12	1	282	279
12	2	258	266
12	3	189	202
12	4	355	353
12	6	278	275
12	7	132	139
13	0	328	332
13	1	169	167
13	2	182	149
13	3	176	169
13	5	171	171
13	6	111	128
14	0	121	119
14	4	97	111
15	1	90	73
16	0	73	77
16	1	84	82
***H =	2****		
0	0	1160	1162
0	1	919	978
0	2	1375	1394
0	3	783	793
0	4	139	147
0	5	620	631
0	6	101	63
0	7	287	288
0	8	349	336
0	10	239	230
0	11	105	90
0	12	124	127
1	0	385	369
1	1	676	675
1	2	972	967
1	3	767	765
1	4	1042	1060
1	5	269	267

K	L	FOBS	FCAL
1	6	414	421
1	7	150	145
1	9	399	393
1	10	259	255
1	11	186	175
1	12	113	110
2	0	93	31
2	1	236	228
2	2	260	256
2	3	1075	1047
2	4	393	390
2	5	374	384
2	7	138	147
2	8	290	278
2	9	271	272
2	10	165	172
2	11	[illegible]	250
3	0	146	152
3	1	258	243
3	2	158	163
3	4	601	604
3	5	151	150
3	6	205	190
3	7	192	178
3	8	94	88
3	9	306	307
3	10	391	389
3	12	165	177
4	0	118	60
4	1	477	479
4	2	515	520
4	3	595	614
4	4	471	465
4	5	168	164
4	6	209	212
4	7	141	150
4	8	379	381
4	9	174	162
4	10	183	177
4	11	177	181
5	0	125	130
5	1	554	564
5	2	635	630
5	3	491	487
5	4	645	642
5	5	217	210
5	6	295	303
5	7	323	312
5	8	168	172
5	9	391	387
5	10	136	137
5	11	125	138
6	0	764	785
6	1	266	269
6	2	799	806
6	3	551	541
6	4	178	176
6	5	382	378
6	6	179	179
6	7	333	332
6	8	307	311
6	10	162	157
6	11	129	134
7	1	526	520
7	2	180	177
7	3	372	370
7	4	581	572
7	5	220	214
7	6	352	344
7	7	238	235
7	9	264	261
7	10	180	173
8	0	345	340
8	1	107	110
8	2	229	226

Table 40 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 2**				1	9	289	282	8	8	131	115	2	6	288	284	9	9	99	127
8	3	261	250	1	10	202	202	8	9	217	215	2	7	263	199	10	0	303	315
8	4	163	173	1	11	171	168	8	10	131	146	2	8	444	442	10	1	180	199
8	5	199	191	2	0	535	533	9	0	223	228	2	9	186	190	10	2	174	180
8	6	225	211	2	1	124	114	9	1	182	177	2	10	162	157	10	3	382	382
8	7	127	138	2	2	594	592	9	2	377	388	2	11	125	129	10	4	139	134
8	8	252	290	2	3	355	326	9	3	92	77	3	0	410	400	10	5	127	130
8	9	112	92	2	4	889	887	9	4	352	349	3	1	372	360	10	6	183	182
8	10	84	90	2	5	247	234	9	6	213	212	3	2	267	263	10	7	103	98
9	1	316	307	2	6	164	155	9	7	187	191	3	3	446	434	10	8	189	190
9	3	92	98	2	7	137	151	9	8	242	230	3	4	358	362	11	0	181	177
9	4	118	121	2	9	367	363	9	9	100	82	3	5	276	282	11	1	217	215
9	5	299	297	2	10	344	339	10	0	153	148	3	6	343	343	11	2	205	204
9	6	133	131	2	11	88	96	10	1	369	371	3	7	189	191	11	3	135	140
9	7	259	254	3	1	131	138	10	2	170	158	3	8	134	123	11	4	226	226
9	8	91	109	3	2	548	565	10	3	153	154	3	9	280	280	11	5	131	146
9	9	106	107	3	3	718	711	10	4	179	182	3	10	211	199	11	6	.58	142
9	10	117	127	3	4	540	526	10	5	136	160	3	11	90	87	11	7	109	112
10	0	306	301	3	5	240	248	10	6	213	188	4	0	130	119	12	2	214	216
10	1	155	147	3	7	171	169	10	7	214	211	4	1	306	297	12	3	183	178
10	2	375	370	3	8	244	242	10	8	148	168	4	2	460	473	12	5	172	162
10	3	220	223	3	9	365	359	10	9	192	192	4	3	550	554	12	7	109	108
10	4	293	292	3	10	88	92	11	0	298	288	4	4	376	386	13	1	162	170
10	5	122	112	3	11	189	188	11	1	128	120	4	5	297	289	13	2	151	194
10	6	233	236	4	0	115	126	11	2	257	254	4	6	266	291	13	3	157	159
10	7	140	129	4	1	587	600	11	3	255	265	4	7	256	251	13	4	161	163
10	8	342	235	4	2	403	402	11	5	117	119	4	8	382	383	14	0	108	116
11	1	363	356	4	3	300	299	11	6	158	166	4	9	158	158	14	2	108	122
11	2	215	200	4	4	641	636	11	7	219	205	4	10	119	123	14	3	163	155
11	3	213	223	4	5	294	287	11	8	231	235	4	11	193	191	14	4	117	101
11	4	306	309	4	6	257	256	12	0	87	89	5	0	69	52	15	0	93	99
11	5	106	93	4	7	142	144	12	1	367	364	5	1	616	610	17	1	127	130
11	6	102	100	4	9	321	317	12	2	175	175	5	2	448	443	***H = 5*****			
11	7	104	107	4	10	236	236	12	3	175	178	5	3	323	344	0	1	672	675
11	8	131	133	5	0	117	113	12	4	215	212	5	4	849	849	0	2	101	98
12	0	335	338	5	1	210	206	12	5	132	130	5	5	305	300	0	4	107	96
12	2	293	294	5	2	673	668	12	6	132	135	5	6	284	196	0	5	273	288
12	3	237	235	5	3	746	743	12	7	143	155	5	7	223	229	0	6	294	284
12	5	166	151	5	4	164	164	13	0	217	215	5	9	233	246	0	7	475	489
12	6	157	139	5	5	211	217	13	2	228	228	5	10	142	151	0	8	118	114
12	7	100	109	5	6	134	136	13	3	186	186	6	0	404	400	0	9	173	168
13	0	206	217	5	7	332	350	13	4	122	120	6	1	285	288	0	11	82	88
13	1	223	221	5	8	439	450	13	6	134	129	6	2	457	465	1	0	682	664
13	2	93	82	5	9	133	128	14	1	119	120	6	3	846	836	1	1	330	331
13	3	128	136	5	10	159	157	14	4	93	113	6	4	123	127	1	2	331	323
13	4	152	154	5	11	108	105	14	5	94	105	6	5	224	238	1	3	184	189
13	5	126	98	6	0	99	99	15	2	84	94	6	6	167	188	1	4	228	240
13	6	146	140	6	1	461	461	15	3	89	93	6	7	217	207	1	5	396	382
13	7	144	148	6	2	261	257	***H = 4*****				6	8	342	338	1	6	809	814
14	0	133	133	6	3	513	518	0	0	435	439	6	9	95	100	1	7	196	203
14	2	89	114	6	4	521	522	0	2	532	524	6	10	112	119	1	8	330	341
14	3	90	92	6	5	143	143	0	3	735	734	7	0	414	428	1	10	157	159
14	4	98	77	6	6	334	326	0	4	124	117	7	1	370	380	1	11	149	153
15	1	85	88	6	7	233	223	0	5	209	196	7	2	391	398	2	0	368	368
15	2	85	80	6	8	247	247	0	6	268	259	7	3	810	813	2	1	720	721
15	3	94	92	6	9	367	371	0	7	271	270	7	4	388	317	2	2	393	390
15	4	82	92	6	10	117	117	0	8	417	422	7	6	272	258	2	3	179	172
H = 3**				6	11	73	36	0	9	147	134	7	7	284	285	2	4	188	140
0	1	329	334	7	0	202	206	0	10	178	159	7	8	97	171	2	5	205	265
0	2	893	894	7	1	279	281	0	11	95	93	7	9	235	255	2	6	293	281
0	3	705	725	7	2	516	526	1	0	199	203	7	10	85	91	2	7	507	498
0	4	890	902	7	3	611	607	1	1	710	717	8	1	293	293	2	9	148	157
0	6	332	314	7	4	346	341	1	2	490	486	8	2	347	343	2	11	81	65
0	8	150	141	7	5	88	131	1	3	335	318	8	3	262	251	3	0	883	890
0	9	519	522	7	6	166	165	1	4	638	622	8	5	259	254	3	1	330	336
0	10	248	244	7	7	241	236	1	5	233	230	8	6	144	149	3	2	416	418
0	11	134	132	7	8	320	300	1	6	219	216	8	7	198	197	3	3	201	204
1	0	459	470	7	9	103	87	1	7	341	334	8	8	208	208	3	4	121	120
1	1	317	317	7	10	88	89	1	9	320	318	8	9	118	130	3	5	336	329
1	2	632	631	8	0	352	347	1	10	109	112	9	1	360	364	3	6	420	419
1	3	1339	1356	8	1	427	429	2	0	67	90	9	2	188	178	3	7	147	155
1	4	341	349	8	2	265	251	2	1	495	489	9	3	142	138	3	8	268	272
1	5	403	389	8	3	109	101	2	2	564	501	9	4	304	301	3	10	134	133
1	6	199	197	8	4	278	256	2	3	537	526	9	5	178	170	4	0	223	221
1	7	224	221	8	5	319	315	2	4	286	275	9	6	151	159	4	1	628	627
1	8	495	501	8	7	198	206	2	8	381	299	9	7	136	148				

Table 40 (continued)

K	L	FOBS	FCAL
H = 5**			
4	2	347	339
4	3	176	172
4	4	295	301
4	5	261	247
4	6	263	263
4	7	333	327
4	8	114	112
4	9	134	143
4	10	110	102
5	0	252	263
5	1	244	255
5	2	155	165
5	3	149	153
5	4	254	236
5	5	464	462
5	6	226	235
5	7	134	130
5	8	250	250
5	10	166	171
6	0	86	107
6	1	297	300
6	2	229	228
6	3	102	102
6	4	292	299
6	6	251	257
6	7	290	283
6	9	150	143
6	10	86	94
7	0	348	354
7	1	319	337
7	2	107	115
7	3	390	384
7	5	336	342
7	6	254	254
7	8	201	211
7	9	96	115
8	0	209	214
8	1	278	281
8	2	470	465
8	4	304	291
8	6	140	150
8	7	208	202
8	8	85	82
8	9	115	126
9	0	137	143
9	1	185	184
9	2	130	124
9	3	277	271
9	4	195	186
9	5	369	310
9	8	130	130
10	0	220	237
10	1	115	108
10	2	243	242
10	4	286	279
10	5	187	175
10	6	181	177
10	7	103	119
11	0	119	108
11	1	241	242
11	3	220	220
11	4	121	105
11	5	261	254
12	1	150	168
12	2	219	220
12	4	190	195
13	0	126	131
13	1	136	127
13	3	103	103
13	4	121	111
14	1	102	93
14	2	128	137
H = 6**			
0	0	765	769
0	1	301	309
0	2	103	100
0	3	161	133
0	5	481	490
0	6	480	460
0	8	119	113
0	10	120	133
1	1	601	605
1	2	176	175
1	3	192	175
1	4	156	149
1	5	333	329
1	6	335	341
1	7	370	367
2	0	808	823
2	1	197	197
2	2	160	174
2	3	111	125
2	4	339	343
2	5	461	460
2	6	465	469
2	7	147	160
2	8	229	223
2	9	124	128
2	10	168	167
3	1	477	494
3	2	181	182
3	3	192	193
3	4	219	218
3	6	275	275
3	7	388	384
3	8	95	90
3	9	162	157
3	10	71	64
4	0	486	496
4	1	462	473
4	2	176	166
4	3	161	150
4	4	193	200
4	5	473	403
4	6	335	338
4	7	106	93
4	8	212	221
4	10	184	187
5	0	324	320
5	1	364	366
5	2	375	364
5	[illegible]	182	185
5	[illegible]	183	188
5	6	229	214
5	7	224	224
5	8	124	128
5	9	116	134
6	0	436	430
6	1	258	256
6	4	220	216
6	5	394	394
6	6	271	268
6	7	103	95
6	8	107	112
7	1	233	222
7	2	206	217
7	3	223	223
7	4	205	196
7	5	185	173
7	6	217	211
7	7	218	219
7	9	107	112
8	0	333	325
8	1	249	251
8	2	123	118
8	3	212	222
8	4	319	320
8	5	391	386
8	6	150	153
8	8	130	131
9	1	228	226
9	2	371	373
9	3	106	99
9	4	280	279
9	6	149	154
9	7	127	126
10	0	149	154
10	1	320	331
10	3	235	218
10	4	155	148
10	5	282	284
10	6	102	84
11	2	170	168
11	4	145	158
11	5	81	44
12	0	164	151
12	1	132	136
12	4	80	93
13	0	120	118
13	1	101	94
13	2	160	163
H = 7**			
0	2	119	127
0	4	274	274
0	6	181	173
0	7	146	148
0	8	88	92
0	9	129	136
1	0	255	260
1	1	202	209
1	2	156	134
1	3	213	208
1	4	262	266
1	5	446	448
1	6	214	213
1	9	86	79
2	1	473	471
2	2	391	385
2	3	214	202
2	4	360	364
2	5	174	164
2	6	230	206
2	7	193	197
2	9	121	120
3	0	574	582
3	1	337	337
3	2	278	278
3	3	310	319
3	4	250	249
3	5	471	470
3	6	163	152
3	7	96	107
3	8	154	174
3	9	89	79
4	0	262	294
4	1	271	263
4	2	339	336
4	3	168	169
4	4	286	278
4	6	247	253
4	7	218	203
4	9	179	184
5	0	239	239
5	1	255	253
5	3	121	108
5	4	159	160
5	5	326	348
5	6	186	183
5	8	189	173
6	1	215	222
6	2	181	166
6	3	145	135
6	4	153	162
6	5	176	189
6	6	184	111
6	7	199	208
7	0	318	320
7	1	173	169
7	2	232	238
7	3	163	156
7	4	149	155
7	5	275	281
7	6	231	228
7	8	141	136
8	1	320	317
8	2	164	175
8	3	124	122
8	4	249	241
8	5	98	103
8	6	121	127
8	7	157	168
9	0	281	285
9	1	118	135
9	2	169	177
9	3	149	157
9	4	175	172
9	5	269	273
9	6	113	105
10	1	191	191
10	2	175	170
10	3	98	95
10	4	105	120
11	0	228	224
12	0	120	117
12	1	120	137
H = 8**			
0	1	140	127
0	3	522	531
0	5	139	149
0	7	85	91
0	8	104	120
1	2	327	320
1	3	134	138
1	4	375	362
2	2	338	334
2	3	323	328
2	4	131	135
2	5	333	327
2	7	160	170
2	8	187	184
3	1	270	275
3	2	267	267
3	3	236	246
3	4	424	425
3	6	204	201
3	8	84	85
4	0	220	218
4	1	130	106
4	2	262	245
4	3	419	416
4	5	220	230
4	7	132	125
4	8	145	140
5	1	165	160
5	2	159	160
5	4	253	240
5	6	164	155
5	7	101	110
6	2	120	120
6	3	129	133
6	5	99	85
6	6	98	124
7	1	192	206
7	3	125	118
7	4	145	147
7	5	161	167
7	6	85	84
8	0	310	307
8	2	273	282
8	3	137	141
8	5	174	178
8	6	98	105
9	1	314	313
9	2	105	100
9	3	136	129
9	4	196	196
10	0	221	215
10	2	176	186
10	3	126	123
11	1	174	171
H = 9**			
0	2	151	145
0	4	245	238
1	0	86	79
1	2	221	217
1	3	351	347
2	1	314	331
2	2	242	250
2	3	153	145
2	4	308	301
2	5	111	112
2	6	90	110
3	0	252	251
3	1	123	112
3	2	378	371
3	3	397	398
3	5	191	185
3	7	204	191
4	0	100	87
4	1	198	203
4	2	147	142
4	3	189	190
4	4	291	278
4	6	138	149
5	1	106	89
5	2	222	219
5	3	219	206
5	4	126	117
5	5	106	85
6	0	102	104
6	2	127	120
6	3	93	91
6	4	102	117
6	5	153	134
7	0	84	85
7	2	212	201
7	3	184	186
7	4	93	92
8	0	92	89
8	1	261	262
8	2	91	80
8	3	116	106
8	4	196	201
9	0	195	191
9	2	230	228
H = 10**			
0	2	161	157
0	3	131	149
0	4	150	126
1	1	191	192
1	5	97	111
2	0	262	262
2	2	274	276
2	3	170	157
2	5	120	116
3	1	309	313
3	2	94	107
3	3	163	161
3	4	190	201
4	0	182	173
4	2	226	224
4	3	211	211
5	0	97	95
5	1	116	122
5	2	140	138
6	1	87	85
6	2	104	101
7	1	111	122
H = 11**			
0	1	117	118
1	0	233	236
2	1	264	270

TABLE 41: ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B
Zr	0.0	0.0	-0.18983(6)	3.01*
S1	-0.1645(2)	-0.0080(2)	-0.0132(1)	4.56*
S2	0.0535(2)	0.1716(1)	-0.2142(2)	4.15*
S3	-0.1851(2)	0.0474(1)	-0.3350(1)	4.33*
C1	-0.0697(7)	-0.0046(7)	0.1207(5)	4.55*
C2	-0.1364(10)	-0.0100(8)	0.2326(6)	7.08*
C3	-0.0686(11)	-0.0036(10)	0.3391(5)	8.76*
C4	-0.0580(7)	0.2186(4)	-0.3220(5)	3.71*
C5	-0.0480(8)	0.3120(5)	-0.3527(6)	5.13*
C6	-0.1351(10)	0.[illegible]6)	-0.4355(7)	6.07*
C7	-0.2330(10)	0.2999(8)	-0.4869(8)	6.57*
C8	-0.2475(8)	0.2068(6)	-0.4570(6)	5.08*
C9	-0.1597(7)	0.1658(5)	-0.3737(5)	3.93*
N	-0.4980(8)	-0.2008(3)	-0.1384(5)	4.45*
C10	-0.3933(9)	-0.2662(8)	-0.1198(14)	10.92*
C11	-0.5023(15)	-0.1388(7)	-0.0264(8)	10.01*
C12	-0.4761(11)	-0.1372(7)	-0.2393(8)	9.07*
C13	-0.6332(9)	-0.2452(6)	-0.1408(10)	7.08*

RIGID BODIES

Atom	x	y	z	B
H1	-0.2398	-0.0170	0.2308	7.90
H2	-0.1198	-0.0085	0.4177	9.60

Table 41 (continued)

Atom	x	y	z	B
D	4.610[a]			
E	1.571			
F	1.571			
H3	0.0269	0.3512	-0.3143	6.20
H4	-0.1241	0.4203	-0.4566	7.00
H5	-0.2981	0.3283	-0.5469	7.90
H6	-0.3209	0.1671	-0.4949	6.30
D	3.391			
E	2.447			
F	3.747			
		HINDERED ROTORS		
H7	-0.3503	-0.2810	-0.1985	11.00
H8	-0.3250	-0.2381	-0.0636	
H9	-0.4316	-0.3238	-0.0827	
BARRIER	0.02[b]			
RADIUS	0.946			
D	0.721			
E	1.373			
F	0.0			
H10	-0.5980	-0.1260	-0.0060	11.00
H11	-0.4537	-0.0797	-0.0446	
H12	-0.4571	-0.1722	0.0416	
BARRIER	0.02			

Table 41 (continued)

ATOM	x	y	z	B
RADIUS	0.946			
D	0.625			
E	3.106			
F	0.0			
H13	-0.3775	-0.1230	-0.2447	9.5
H14	-0.5275	-0.0785	-0.2238	
H15	-0.5078	-0.1674	-0.3144	
BARRIER	0.02			
RADIUS	0.946			
D	0.676			
E	6.091			
F	0.0			
H16	-0.6652	-0.2550	-0.0568	8.0
H17	-0.6972	-0.2034	-0.1853	
H18	-0.6265	-0.3065	-0.1838	
BARRIER	0.02			
RADIUS	0.946			
D	0.444			
E	4.689			
F	0.0			

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*Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 42.

[a] D, E, and F are as described for Table 32.

[b] BARRIER (Bd) is the relative barrier to rotation of the hindered rotor group. Bd = $V_o/2kT$, where V_o = potential barrier to rotation (kcal mol^{-1}).

TABLE 42: ANISOTROPIC THERMAL PARAMETERS (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0369(4)	0.0467(4)	0.0309(3)	0.0033(5)	0.0	0.0
S1	0.0519(10)	0.0724(12)	0.0491(8)	-0.0014(13)	0.0142(8)	-0.0058(13)
S2	0.0503(10)	0.0535(9)	0.0536(10)	-0.0022(8)	-0.0099(8)	0.0043(8)
S3	0.0479(10)	0.0663(10)	0.0502(10)	0.0035(9)	-0.0149(9)	-0.0029(8)
C1	0.093(5)	0.042(3)	0.038(3)	-0.021(6)	0.013(3)	-0.003(5)
C2	0.134(8)	0.080(6)	0.055(4)	-0.051(6)	0.042(5)	-0.029(5)
C3	0.200(12)	0.096(5)	0.036(3)	-0.065(11)	0.021(4)	-0.015(7)
C4	0.049(4)	0.055(4)	0.038(3)	0.009(3)	0.004(3)	0.005(3)
C5	0.074(6)	0.061(4)	0.060(4)	0.011(4)	0.012(4)	0.009(4)
C6	0.080(6)	0.080(6)	0.071(5)	0.033(5)	0.011(5)	0.024(5)
C7	0.081(7)	0.116(7)	0.052(5)	0.044(6)	-0.004(5)	0.026(6)
C8	0.058(5)	0.088(6)	0.047(4)	0.022(4)	-0.012(4)	0.014(5)
C9	0.049(4)	0.070(4)	0.030(3)	0.018(4)	0.005(3)	0.002(3)
N	0.042(3)	0.054(3)	0.073(3)	-0.005(4)	-0.000(5)	0.017(3)

Table 42 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C10	0.048(6)	0.110(8)	0.257(16)	0.028(5)	0.031(8)	0.081(10)
C11	0.153(10)	0.113(7)	0.114(7)	-0.049(9)	-0.003(11)	-0.018(6)
C12	0.083(8)	0.137(8)	0.124(7)	-0.012(6)	0.006(6)	0.075(7)
C13	0.063(6)	0.095(7)	0.111(8)	-0.018(5)	-0.009(6)	0.032(6)

TABLE 43: INTRA-IONIC CONTACTS (Å)

ATOMS	DISTANCE (Å)	ATOMS	DISTANCE (Å)
Zr-S1	2.555(2)	Zr-S2	2.537(2)
Zr-S3	2.538(2)	S2-S3	3.255(2)
S1-S1'	3.275(3)	S1-S2'	3.424(3)
S2-S3'	3.662(2)	S1-S3	3.665(2)
S1-C1	1.759(6)	S2-C4	1.764(6)
S3-C9	1.772(7)	C1-C1'	1.391(14)
C1-C2	1.410(8)	C2-C3	1.364(11)
C3-C3'	1.366(22)	C4-C5	1.388(9)
C5-C6	1.389(10)	C6-C7	1.355(13)
C7-C8	1.386(11)	C8-C9	1.400(9)
C9-C4	1.388(9)	N-C10	1.416(10)
N-C11	1.530(10)	N-C12	1.462(9)
N-C13	1.487(10)		

TABLE 44: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLE	ATOMS	ANGLE
S1-Zr-S1'	79.74(8)	S2-Zr-S3	79.80(6)
S1-Zr-S3	92.06(6)	S1-Zr-S2'	84.51(7)
S3-Zr-S2'	92.40(6)	S3-Zr-S3'	101.19(8)
S1-Zr-S2	105.03(7)	S2-Zr-S2'	167.76(8)
S1-Zr-S3'	159.80(7)	Zr-S1-C1	107.7(2)
Zr-S2-C4	108.2(2)	Zr-S3-C9	108.0(2)
S1-C1-C1'	122.4(2)	S2-C4-C9	121.9(5)
S3-C9-C4	121.8(5)	C1'-C1-C2	118.2(5)
C1-C2-C3	121.8(9)	C2-C3-C3'	119.9(6)
C9-C4-C5	118.6(6)	C4-C5-C6	121.4(7)
C5-C6-C7	119.6(8)	C6-C7-C8	120.7(8)
C7-C8-C9	119.9(8)	C8-C9-C4	119.8(6)
C10-N-C11	106.8(10)	C10-N-C12	114.7(8)
C10-N-C13	112.4(6)	C11-N-C12	105.1(6)
C11-N-C13	103.8(8)	C12-N-C13	112.9(7)
S2'-S1-S3	62.10(5)	S2'-S3-S1	55.71(5)
S1'-S2-S3'	62.19(5)		

TABLE 45: INTER-IONIC CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE (Å)
S2	H5	$1/2+x, 1/2-y, \bar{z}-1$	3.031
S2	C10	$\bar{x}, \bar{y}, z$	3.786(9)
S3	H2	$x, y, z-1$	2.930
S3	C12	$\bar{x}-1, \bar{y}, z-1$	3.756(11)
C1	C10	$1/2-x-1, 1/2+y, \bar{z}$	3.446(15)
C1	C13	$1/2+x, 1/2-y-1, \bar{z}$	3.657(13)
C1	C10	$1/2+x, 1/2-y-1, \bar{z}$	3.730(15)
C2	C13	$1/2+x, 1/2-y-1, \bar{z}$	3.662(14)
C2	C10	$1/2-x-1, 1/2+y, \bar{z}$	3.733(17)
C3	C6	$1/2-x-1, 1/2+y-1, \bar{z}$	3.754(12)
C4	H5	$1/2+x, 1/2-y, \bar{z}-1$	3.036
C4	C13	$\bar{x}-1, \bar{y}, z$	3.687(12)
C5	H6	$1/2+x, 1/2-y, \bar{z}-1$	2.832
C5	C8	$1/2+x, 1/2-y, \bar{z}-1$	3.666(10)
C8	C13	$\bar{x}-1, \bar{y}, z$	3.745(13)
C8	C12	$\bar{x}-1, \bar{y}, z$	3.792(13)
C9	C13	$\bar{x}-1, \bar{y}, z$	3.494(12)

TABLE 46: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Zr, S1, S3

EQUATION OF PLANE: $0.5985X - 0.2147Y - 0.7718Z = -1.6254$ [a]

(B) ATOMS FORMING PLANE: Zr, S1, S1'

EQUATION OF PLANE: $-0.0622X + 0.9978Y = 0.0$

(C) ATOMS FORMING PLANE: S2, S3, C4, C5, C6, C7, C8, C9.

EQUATION OF PLANE: $0.6201X - 0.2685Y - 0.7372Z = -1.4221$

DISTANCES OF ATOMS FROM PLANE (Å);

S2	0.000(3)	C6	0.014(12)
S3	0.002(3)	C7	-0.013(14)
C4	-0.032(10)	C8	-0.016(15)
C5	-0.015(11)	C9	0.044(15)
Zr	-0.1303(8)		

(D) ATOMS FORMING PLANE: S2, S2', C1, C1', C2, C2', C3, C3'

EQUATION OF PLANE: $-0.0717X + 0.9974Y = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S1	0.003(3)	C2	-0.046(13)
S1'	-0.003(3)	C2'	0.046(13)
C1	-0.016(10)	C3	0.044(15)
C1'	0.016(10)	C3'	-0.044(15)

(E) ATOMS FORMING PLANE: S1, S3', S2'

EQUATION OF PLANE: $0.9176X + 0.3961Y - 0.03372Z = -1.5424$

Table 46 (continued)

[a] X, Y, and Z are in Å and refer to the orthogonal coordinates along *a*, *b* and *c**.

TABLE 47: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE (DEGREES)
(1) Zr, S2, S3	Zr, S2', S3'	101.1
(2) Zr, S2, S3	Zr, S1, S1'	104.7
(3) Zr, S2, S3	S2, S3, C4, C5, C6, C7, C8, C9	3.9
(4) Zr, S1, S1'	S1, S1', C1, C1', C2, C2', C3, C3'	0.5
(5) S2, S3, C4, C5, C6, C7, C8, C9	S2', S3,', C4', C5', C6', C7', C8', C9'	95.0
(5) S2, S3, C4, C5, C6, C7, C8, C9	S1, S1', C1, C1', C2, C2', C3, C3'	108.2

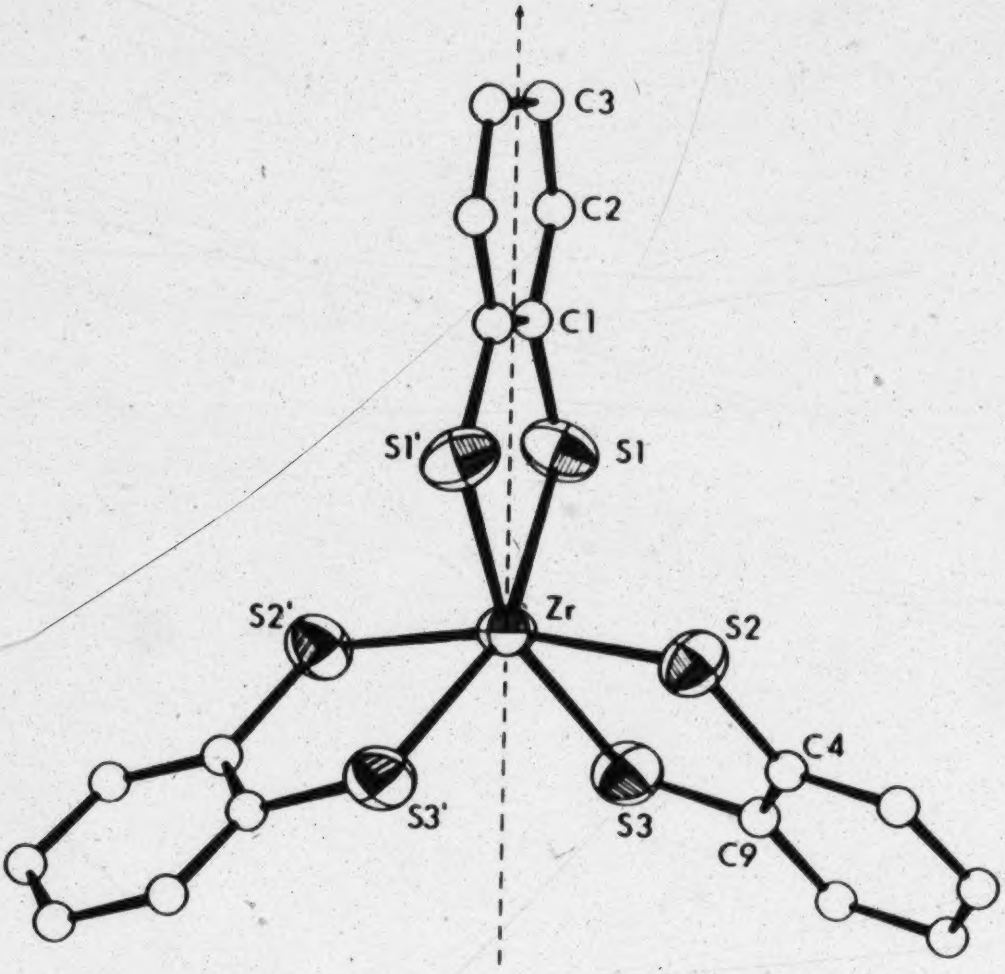

C3
C2
C1
S1'
S1
Zr
S2'
S2
C4
S3'
S3
C9

Fig. 17: A Perspective View of the $Zr(S_2C_6H_4)_3^{2-}$ Dianion, Viewed Down the Approximate Molecular 3-Fold Axis.

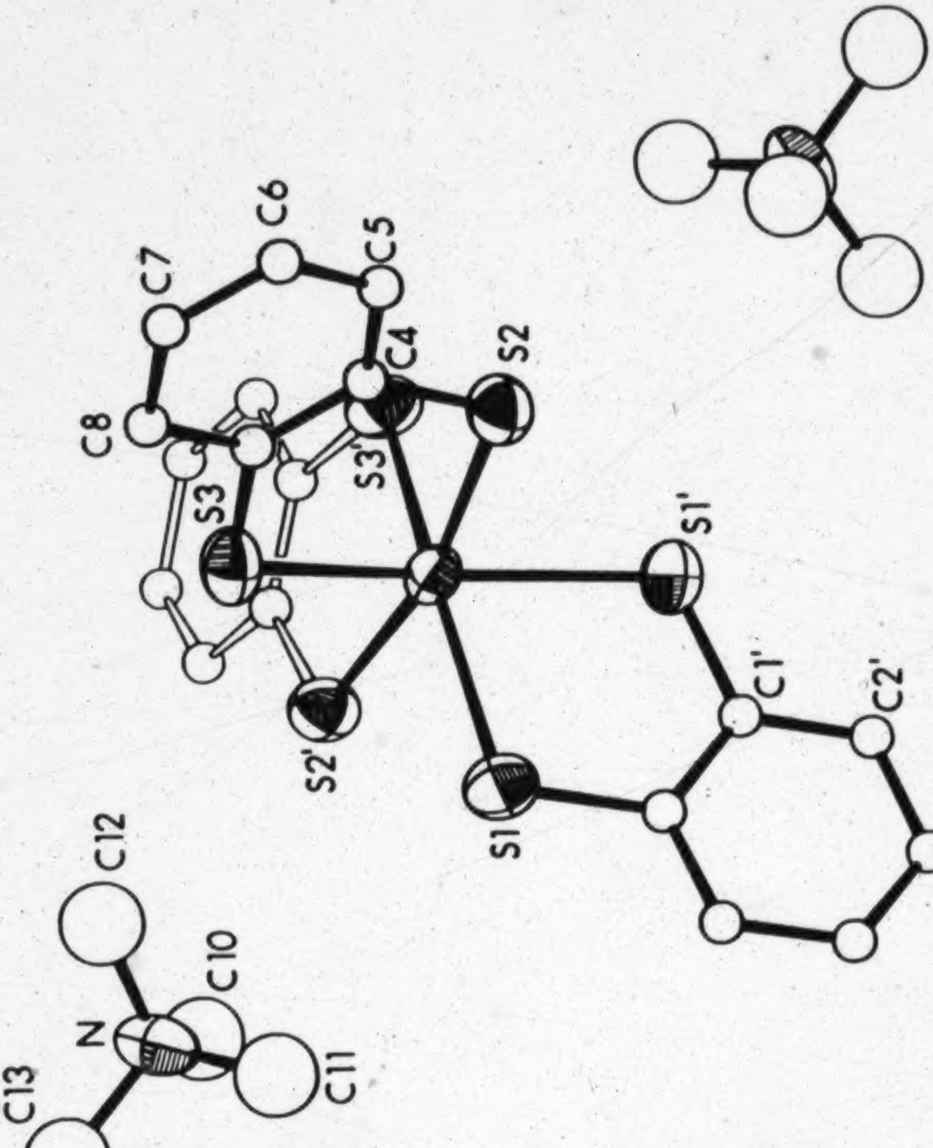

C13
N
C12
C10
C11
S2'
S1
C1'
C2'
C3'
S1'
S3
S3'
C8
C4
C7
C6
C5
S2

Fig. 18: A Perspective View of $[N(CH_3)_4]_2[Zr(S_2C_6H_4)_3]$

DESCRIPTION OF STRUCTURE

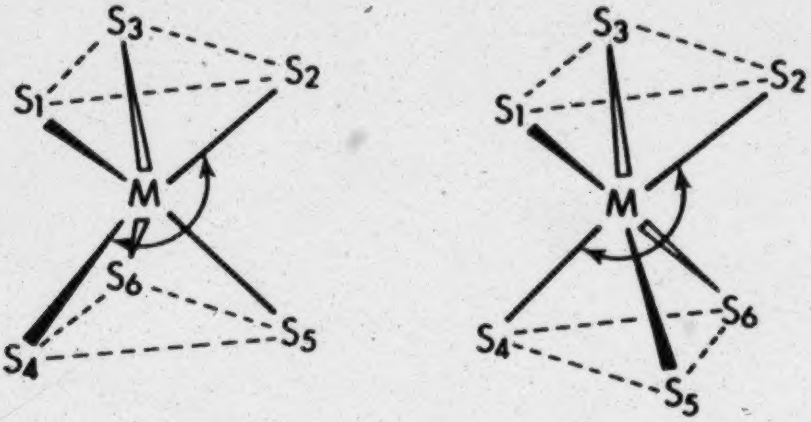
The $Zr(bdt)_3^{2-}$ dianion, viewed down its approximate three-fold axis, is shown in Fig. 17, and the dianion and the two tetramethylammonium cations are shown in Fig. 18. The dianion is located on the crystallographic two-fold axis whereas the tetramethylammonium cations sit in general positions.

In the dianion, the six sulfur atoms are approximately equidistant from the zirconium atom and form a coordination polyhedron which is intermediate between an octahedron and a trigonal prism. Since the $ZrS_2C_6H_4$ fragments are approximately planar, the symmetry of $Zr(bdt)_3^{2-}$ approximates D_3. The dithiolene ligands radiate from the zirconium atom in a "propeller-like" arrangement as opposed to the "paddle-wheel" arrangement in the trigonal prisms.

In describing the degree of distortion of the metal coordination from either of the trigonal prismatic or octahedral limits, two parameters are especially useful; the S-M-S angles involving sulfur atoms which are almost *trans* to each other, and the projection angle between the two triangular faces of the prism (trigonal twist angle).

In a regular trigonal prism the S-M-S angle between pseudo *'trans'* sulfur atoms is approximately

136°. In an octahedron this angle is 180°. These two extremes are shown in Fig. 19, the S2-M-S4 angle being the angle of interest. However, for an



TRIGONAL PRISM

OCTAHEDRON

Fig. 19. *Trans* S-M-S Angles in the Trigonal Prism and the Octahedron.

intraligand S-Zr-S angle of ~ 80°, considering only the geometric constraints of the ligand, a *trans* S-Zr-S angle of 170° is obtained as the corrected octahedral limit.[161] The values observed for the Zr(bdt)$_3^{2-}$ dianion [167.76(8)° and 159.80(7)°] are thus closer to the octahedral limit and on this basis the zirconium coordination can be described as distorted octahedral. The non-equivalence of these two independent values indicates that the distortion is not regular and that one ligand (containing S1 and S1') is rotated more towards the trigonal prismatic structure than the other two ligands.

The other indication of the degree of distortion from the prismatic or octahedral limits is the trigonal twist or projection angle shown in Fig. 20. In the trigonal prism where the two triangular faces are eclipsed, this angle equals 0°, whereas in the ideal octahedron this angle is 60°. Again however, because of the constraint of ligand bite in these bidentate ligands, the octahedral limit is not attained. Rather, this angle will be limited by the ratio of intra-

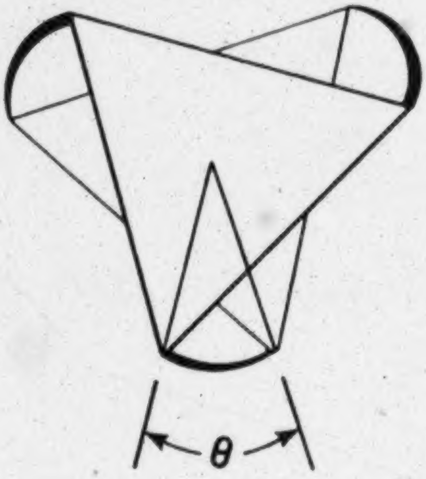


Fig. 20. Trigonal Twist Angle Projected Perpendicular to the Molecular 3-Fold Axis.

ligand S-S distances to the M-S distances. For the $Zr(bdt)_3^{2-}$ dianion, this ratio (1.284) predicts[166] (on the basis of minimizing interligand repulsions) a twist angle of approximately 48° for the corrected octahedral limit. An average twist angle in this structure is calculated at 37° using equilateral triangles that correspond to a best fit with the observed individual atom coordinates. Thus the twist angle differs from the corrected octahedral limit by only 11°. By comparison, in the structure[167] of $Al(O_2C_7H_5)_3$, the observed trigonal twist angle (48.1°) is essentially that calculated using the constraints of ligand bite and this appears typical of structures where the only factor favouring the prism is minimization of the interligand repulsions. Thus the deviation of 11° from the corrected octahedral limit is significant and indicates a genuine tendency towards trigonal prismatic coordination in this structure.

The Zr-S distances (av. 2.543 Å) are longer than those observed in the molybdenum and niobium *tris* (benzene dithiol) complexes (see Table 48) and thus complete a trend through this series with the metal-sulfur distances increasing approximately as predicted by their covalent radii.[133] As with the niobium complex, the metal-sulfur distances again contain irregularities of statistical significance. The Zr-S distance within the ligand bisected by the two-fold axis [2.555(2) Å] is longer than the other two independent Zr-S distances [2.537(2) Å and 2.538(2) Å].

Although this complex is of considerable interest in relation to the other *tris* dithiolenes, it is also interesting in its own right. The number of structurally characterized six coordinate zirconium complexes is small[168] and indeed $[N(CH_3)_4]_2[Zr(bdt)_3]$ is believed to be the first example of a six coordinate zirconium-sulfur complex. The observed Zr-S distances lie midway between the values 2.49 Å and 2.58 Å, corresponding to the sums of the covalent and ionic (Zr^{4+} and S^{2-}) radii[133,169] respectively.

The intraligand S-Zr-S angles (av. 79.77°) are slightly less than those observed in $Mo(bdt)_3$ and $Nb(bdt)_3^-$ (82.12° and 80.35° respectively) and complete a trend through the series. This trend is due to the relatively fixed ligand bite which does not increase as rapidly as the metal-sulfur distances.

The S-C distances seem to be an excellent indication of the tendency of the ligand towards either the oxidized or reduced formulations. In $Zr(bdt)_3^{2-}$ the average S-C distance (1.765 Å) is very close to that predicted for a single bonded sulfur-carbon distance (1.77 Å).[84,133] Thus the ligand geometry approximates that corresponding to the dithiolato formulation and the formal oxidation state of (IV) appears to be a reasonable description for the zirconium atom in this structure. This structure is important in demonstrating that the ligand can attain the dithiolato limit. The carbon-carbon distances within the ligands (av. 1.384 Å) are close to those observed in benzene.[158] However, as in the molybdenum and niobium complexes, shortening of the C_C-C_D bond is observed (see Fig. 21), probably due to thermal motion of the rings. In addition, in ligand 1, which is bisected by the crystallographic two-fold axis, the bond lengths vary significantly throughout the ring. One worrying feature of this ring is the presence of anomalously high thermal parameters (U_{11}'s) of the carbon atoms. This seems to indicate either a disorder or a systematic error is present. The disorder could correspond to the non-equivalence of Zr-S1 and Zr-S1' distances for a particular model. However, this problem is unlikely to affect the general conclusions of this study. The C-C bond lengths within the rings are therefore unreliable and no chemical significance should be placed on their

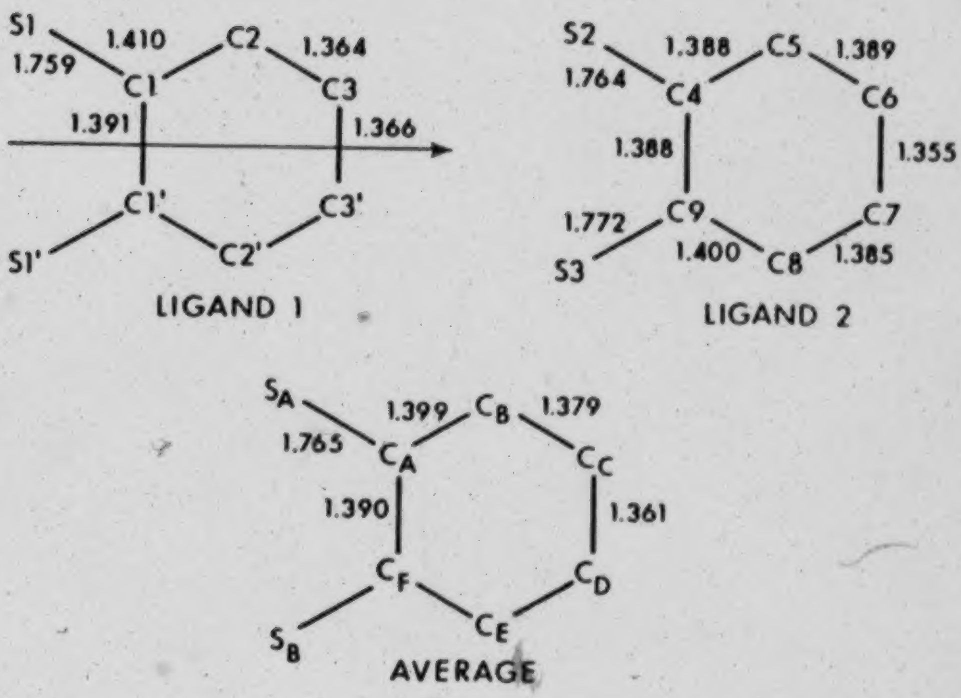

S1
1.759
1.410
C2
1.364
C1
C3
1.391
1.366
C1'
C3'
S1'
C2'
LIGAND 1
S2
1.764
1.388
C5
1.389
C4
C6
1.388
1.355
1.772
C9
C7
S3
1.400
C8
1.385
LIGAND 2
S_A
1.765
1.399
C_B
1.379
C_A
C_C
1.390
1.361
C_F
C_D
S_B
C_E
AVERAGE

Fig. 21: Dimensions Within the Dithiolene Ligands.

differences.

The interligand S-S distances are, as expected, much longer than the intraligand distances, this due merely to the distortion towards the octahedron which maximizes the interligand separations. In addition the intraligand S-S distances in $Zr(bdt)_3^{2-}$ are longer than those in $Mo(bdt)_3$ and $Nb(bdt)_3^{-}$, and are due to increasing S-C distances through the series. The

TABLE 48: SELECTED DISTANCES (Å) FOR
FOR *TRIS*(1,2-DITHIOLENE) COMPLEXES

COMPOUND	M-S	S-S (INTRA)	S-S (INTER)	S-C	REFERENCE
$Re(S_2C_2Ph_2)_3$	2.325(4)	3.032(10)	3.050(8)	1.69[a]	129
$Mo(S_2C_2H_2)_3$	2.33(1)	3.10	3.11	1.70(3)	130
$V(S_2C_2Ph_2)_3$	2.338(4)	3.060(6)	3.065	1.69(1)	132
$V[S_2C_2(CN)_2)_3^{2-}$	2.36(1)	3.13(2)	3.20	1.72(2)	140
$Mo[S_2C_2(CN)_2]_3^{2-}$	2.373(4)	3.113	3.188	1.74(1)	141,170
$W[S_2C_2(CN)_2]_3^{2-}$	2.371(5)	3.112	3.193	1.73(2)	170
$Fe[S_2C_2(CN)_2]_3^{2-}$	2.261(2)	3.147(2)	3.19	1.731(4)	142
$In[S_2C_2(CN)_2]_3^{3-}$	2.604(8)	3.40(1)	3.89(1)	1.72(3)	171
$Mo(S_2C_6H_4)_3$	2.367(2)	3.110(3)	3.091(2)	1.727(6)	THIS WORK
$Nb(S_2C_6H_4)_3^-$	2.441(2)	3.150(3)	3.232(3)	1.744(7)	"
$Zr(S_2C_6H_4)_3^{2-}$	2.543(2)	3.265(3)	3.584(2)	1.765(6)	"

[a] Where standard deviations are not shown, they were not given in the original paper. In $Re(S_2C_2Ph_2)_3$ the standard deviations are not shown due to a wide range in S-C distances.

TABLE 49: SELECTED ANGLES FOR *TRIS* (1,2-DITHIOLENE) COMPLEXES (DEGREES)

COMPOUND[d]	S-M-S (INTRA)	S-M-S (TRANS)	PROJECTION ANGLE[c]	DIHEDRAL MS_2/LIGAND ANGLE	COORDINATION
$Re(S_2C_2Ph_2)_3$	81.4(4)	-136	<1	--	TRIGONAL PRISM
$Mo(S_2C_2H_2)_3$	82.5	-136	0	18	"
$V(S_2C_2Ph_2)_3$	81.7(2)	-136	8.5 [a]	--	"
$V[S_2C_2(CN)_2]_3^{2-}$	--	158.6	TWISTED [b]	--	DISTORTED OCTAHEDRON
$Mo[S_2C_2(CN)_2]_3^{2-}$	82.3(2)	156	28	-2	"
$W[S_2C_2(CN)_2]_3^{2-}$	82.1(2)	156	28	-2	"
$Fe[S_2C_2(CN)_2]_3^{2-}$	88.0(1)	--	-60	--	OCTAHEDRON
$In[S_2C_2(CN)_2]_3^{3-}$	81.5(3)	169.3(3)	--	--	DISTORTED OCTAHEDRON
$Mo(S_2C_6H_4)_3$	82.18(8)	135.70(7)	0	13.1,21.1, 30,0	TRIGONAL PRISM
$Nb(S_2C_6H_4)_3^-$	80.35(7)	135.06(7)	0.7	22.4	TRIGONAL PRISM
$Zr(S_2C_6H_4)_3^{2-}$	79.77(7)	163.78(8)	37.0	3.9,0.5	DISTORTED OCTAHEDRON

[a] Calculated in ref. 172 from atomic coordinates given in original paper.

[b] No coordinates or twist angle given.

[c] Trigonal twist angle projected perpendicular to molecular 3-fold axis.

[d] References shown in Table 48.

S-C-C and C-C-C angles within the ligands are all close to the expected value of 120°.

An interesting feature observed in $Mo(bdt)_3$ and isoelectronic $Nb(bdt)_3^-$ is the large bend of the MS_2 planes from the ligand S_2C_6 planes (21.4° and 22.4° respectively). This had also been observed in $Mo(S_2C_2H_2)_3$[130] and $Mo[Se_2C_2(CF_3)_2]_3$[152] but was not observed in $Re(S_2C_2Ph_2)_3$[129] or $V(S_2C_2Ph_2)_3$.[132] In $Zr(bdt)_3^{2-}$ these planes are approximately coplanar, the dihedral angles between ZrS_2 and S_2C_6 planes being 3.9° and 0.5°. Although Schrauzer had attributed[138] the bend observed in $Mo(S_2C_2H_2)_3$ as due to hybridization of the sulfur atoms between sp^2 and sp^3, it is then difficult to account for the near planarity of the ligands in the zirconium, rhenium and vanadium complexes.

Comparison of the angular parameters in Table 49 allows the complexes to be placed in order of increasing tendency toward the trigonal prismatic structure. Consideration must be given to the general criticism of X-ray crystallographic studies, that one cannot guarantee that the observed geometry corresponds to the ground state. Thus the differences between $V(mnt)_3^{2-}$ and $Mo(mnt)_3^{2-}$ [or $W(mnt)_3^{2-}$] may not be significant. The order for the dianionic species is then:

corrected octahedral limit $\simeq \mathrm{Fe(mnt)}_3^{2-} < \mathrm{Zr(bdt)}_3^{2-} <$

$\mathrm{V(mnt)}_3^{2-}$
$\mathrm{Mo(mnt)}_3^{2-}$ $\ll$ trigonal prismatic limit
$\mathrm{W(mnt)}_3^{2-}$

The corresponding order for the isoelectronic series, as described in this thesis is:

corrected octahedral limit $< \mathrm{Zr(bdt)}_3^{2-} \ll \mathrm{Nb(bdt)}_3^{-} \leq \mathrm{Mo(bdt)}_3$

$=$ trigonal prismatic limit.

Chapter IX presents a general rationalization for these trends.

A perspective view of the dianion and the tetramethylammonium cations is shown in Fig. 18. As expected the cations are close to tetrahedral, with the small distortions present being due to packing effects. The average N-C distance (1.474 Å) agrees quite well with that predicted (1.47 Å) assuming single bonded covalent radii.[133] This value is also in good agreement with previous structural determinations in which the tetramethylammonium cation was involved.[173,174]

CHAPTER IX: TRIGONAL PRISMATIC *vs.* OCTAHEDRAL COORDINATION IN *TRIS* (1,2-DITHIOLATO) COMPLEXES

The isoelectronic series of *tris* (1,2-dithiolato) complexes, described in the latter part of this thesis, show dramatic changes in the coordination polyhedron. These changes, from an almost perfect trigonal prism in the neutral molybdenum complex, to a very slightly distorted trigonal prism in the niobium complex anion, to a distorted octahedron in the zirconium complex dianion, are accompanied by smooth increases in metal-sulfur distances, sulfur-carbon distances, and inter-ligand sulfur-sulfur distances (see Table 48). These changes correspond to the increasing importance of the dithiolato formulation for the ligand, that is, $S_2C_6H_4^{2-}$. The increase in interligand sulfur-sulfur distances would lead to a reduction in direct sulfur-sulfur bonding, which has been postulated as a factor in stabilizing the prism.[137,138,170] In this chapter the structural trends are correlated with molecular orbital energy level diagrams.

Two energy level schemes have been presented to account for the stability of the prism in certain *tris* (1,2-dithiolato) complexes. One of these schemes, due to Schrauzer and Mayweg[138] (which will be referred to as scheme 1) is presented for an unspecified first

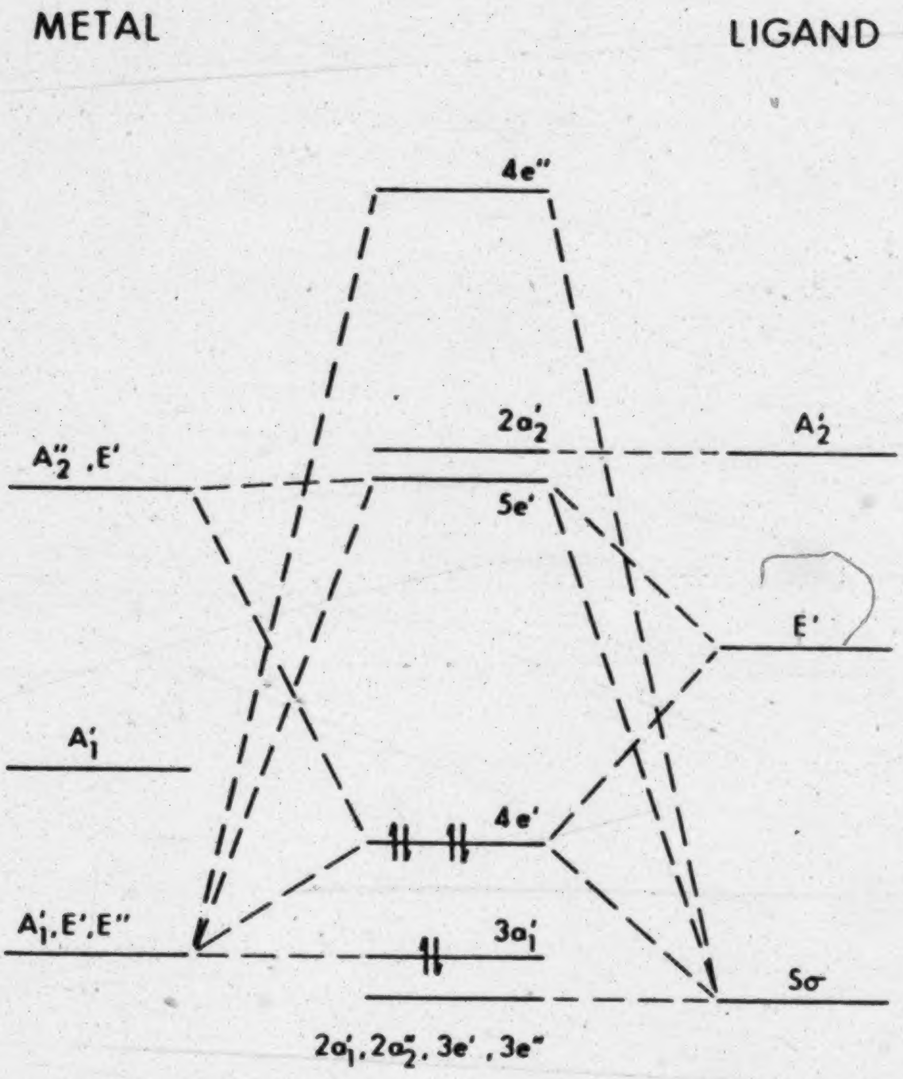

METAL
LIGAND
4e"
2a$_2'$
A$_2'$
A$_2''$,E'
5e'
E'
A$_1'$
4e'
A$_1'$,E',E"
3a$_1'$
Sσ
2a$_1'$,2a$_2''$, 3e' ,3e"

FIG. 22: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY G. N. SCHRAUZER AND V. P. MAYWEG

transition series element. The important levels of this scheme are shown in Fig. 22. The alternative scheme, due to Gray *et. al.*[137] (which will be referred to as scheme 2), is shown in Fig. 23. The differences between the two schemes arise, in part, from the relative positions of the metal and ligand orbitals.[132] Both schemes agree on the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} orbitals with appropriate combinations of ligand π orbitals (symmetry b_1 for an isolated ligand) to give bonding 4e' and antibonding 5e' levels. Scheme 2, however, proposes an additional significant interaction between the metal d_{z^2} orbital and ligand non-bonding sigma orbitals, giving one bonding ($2a_1'$) and one antibonding ($3a_1'$) level. Scheme 1 has also been challenged on the basis of electron spin resonance studies,[132,175] and can be shown to be inconsistent with the electronic spectra in this series of compounds. Specifically it predicts an increase in the frequency that would correspond to the transitions $3a_1' \rightarrow 5e''$ and $3a_1' \rightarrow 2a_2'$ when comparing the niobium complex with the molybdenum complex, which is the opposite of the experimental results (Table 18). Scheme 2 correctly predicts the experimental observations, as Gray *et. al.*[137] attribute the transitions as due to $2a_2''(\pi_h)$, $3e'(\pi_h) \rightarrow 3a_1'(d_{z^2})$.

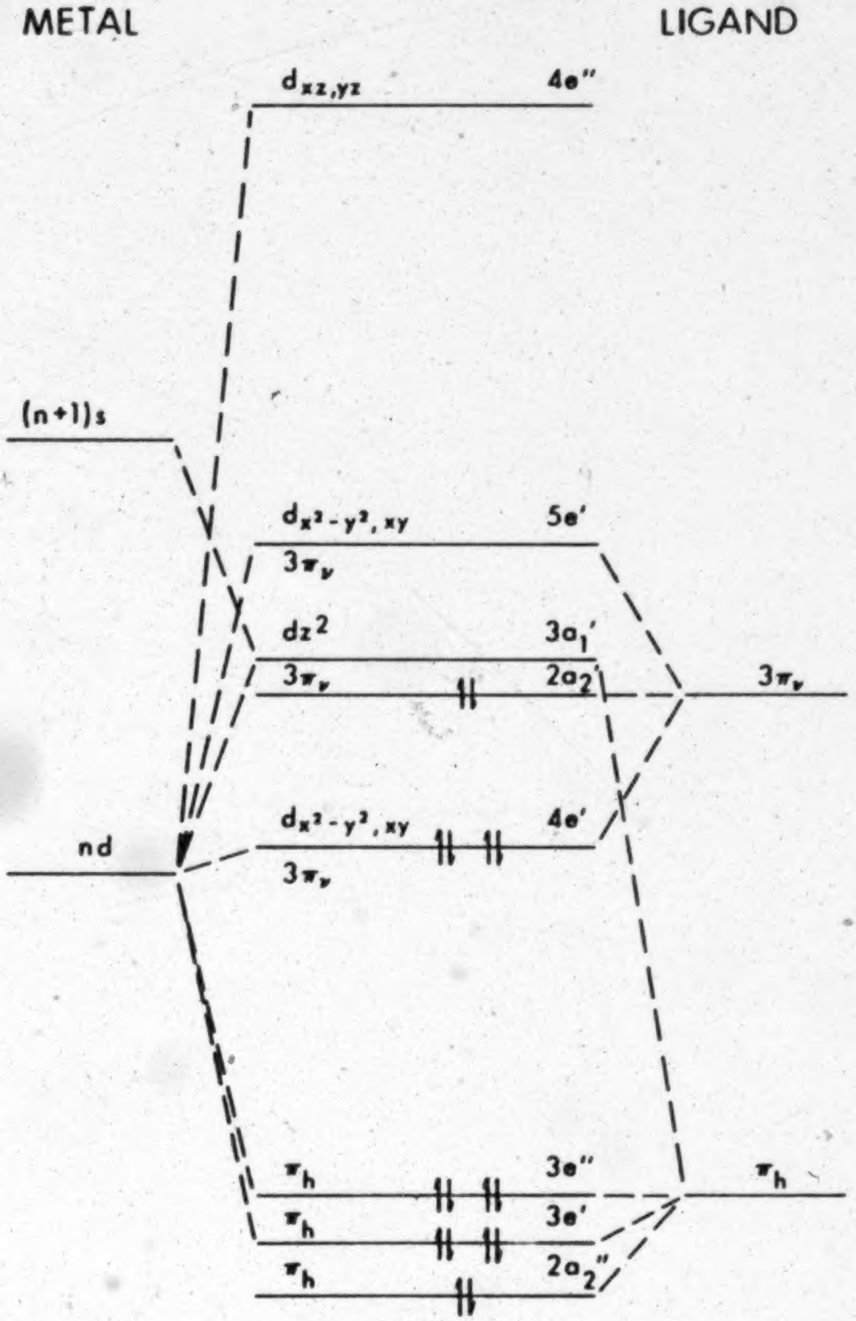

METAL
LIGAND
$d_{xz,yz}$
4e″
(n+1)s
$d_{x^2-y^2,xy}$
5e′
$3\pi_v$
dz^2
$3a_1'$
$3\pi_v$
$2a_2'$
$3\pi_v$
nd
$d_{x^2-y^2,xy}$
4e′
$3\pi_v$
π_h
3e″
π_h
π_h
3e′
π_h
$2a_2''$

FIG. 23: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY H. B. GRAY *et. al.*

Since scheme 2 seems more consistent with the experimental results, it is favoured over scheme 1, and therefore will be used in all subsequent discussions. In this M.O. description (Fig. 23), the levels $2a_2''$, $3e'$ and $3e''$ consist mainly of sulfur sp^2 hybrid orbitals (π_h) at 120° to the σ orbitals pointing at the metal. The $2a_2'$ orbital is non-bonding and the $3a_1'$ is principally metal in character, having symmetry d_{z^2}. The $4e'$ and $5e'$ are both metal ($d_{x^2-y^2}, d_{xy}$) and ligand ($3\pi_v$) in character and both are strongly delocalized over the metal and ligands. Stability of the prism was postulated, by Gray *et. al.* as due to interaction of the sulfur π_h orbitals with the metal d_{z^2} orbital producing the stable bonding orbital $2a_1'$, which is always filled; also the interaction of the metal $d_{x^2-y^2}$ and d_{xy} orbitals with the $3\pi_v$ ligand orbitals produces the stable $4e'$ orbitals which are also filled in these complexes.

In order to use the M.O. scheme by Gray *et. al.* it must be shown that it will apply to the series of interest in this thesis. Considering the ligand and metal orbitals separately, it can first be shown that the energy levels of the molybdenum 4d and rhenium 5d orbitals are similar.[176] Therefore use of the molybdenum atom instead of rhenium in scheme 2 is justified.

The energy levels of the ligands $S_2C_2H_2$ and $S_2C_6H_4$ can be compared using the calculations of Birss and Das Gupta.[160] The π orbitals for these ligands, the calculated orbital energies and geometries are presented in Figs. 24, 25 and 26. Each ligand is shown in the reduced form (corresponding to the dithiolato limit) and in the neutral or oxidized form (2 π electrons less). The π orbitals of particular interest are the $2b_1$ for $S_2C_2H_2$ and $3b_1$ for $S_2C_6H_4$. Comparing the oxidized forms of the ligands, the energies of the $2b_1$ ($S_2C_6H_2$) and $3b_1$ ($S_2C_6H_4$) levels are -16.4 e.v. and -15.3 e.v. respectively. A comparison of the reduced forms of the ligands shows the energies are -10.2 e.v. and -10.0 e.v. for the same levels. The probable error in these energy levels is of the order of 0.3 e.v.. Thus it is clear that the molecular orbital scheme proposed for $Re(S_2C_2H_2)_3$ should closely approximate that used for $Mo(S_2C_6H_4)_3$, because of the near equality of both metal and ligand orbital energies.

As postulated by Gray *et. al.*,[137] the stability of the prism is due, in part, to the interaction of the ligand $3\pi_v$ and metal $d_{x^2-y^2}$ and d_{xy} orbitals, producing the 4e' orbital. The series, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$, permits examination of this

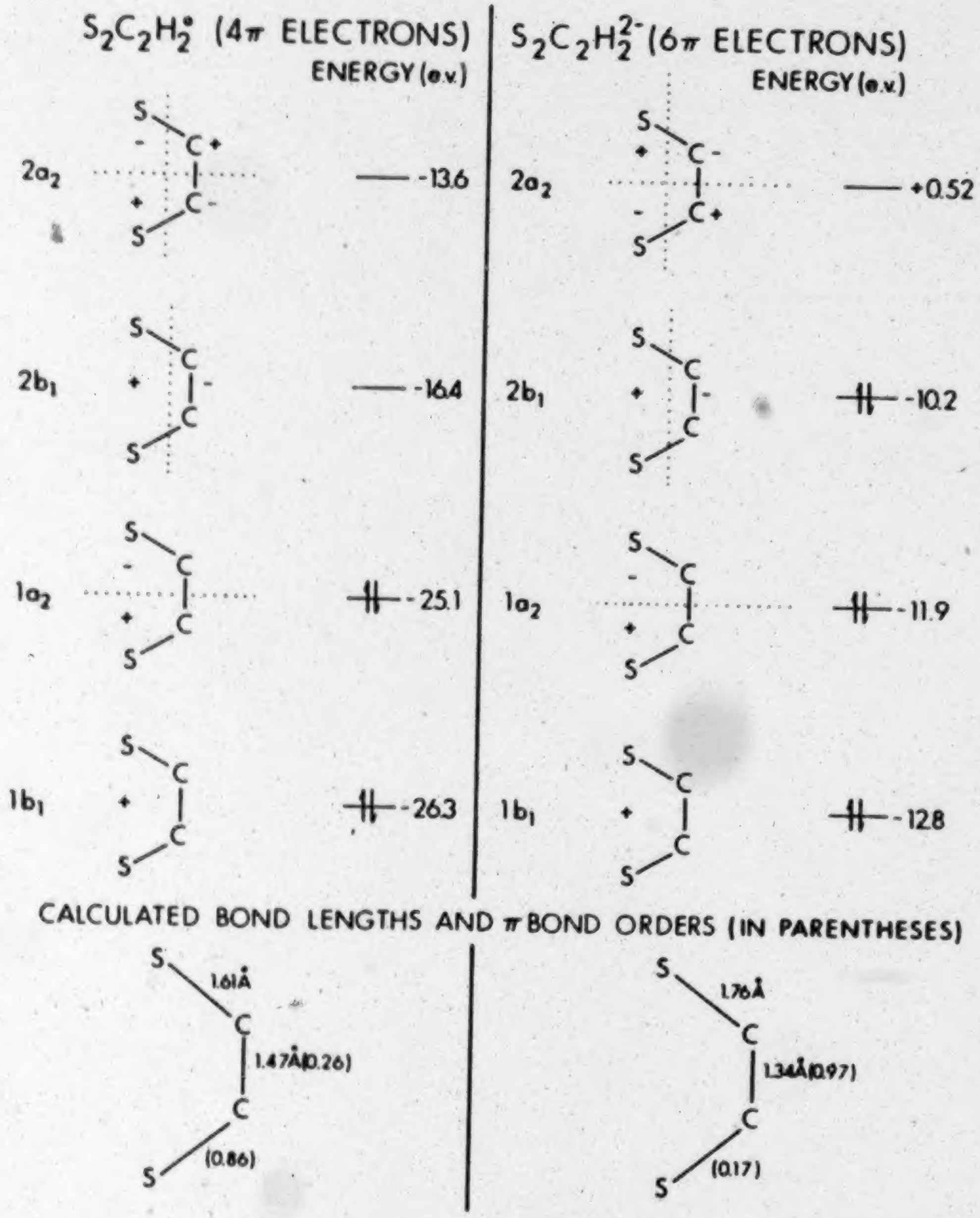

S₂C₂H₂• (4π ELECTRONS)
ENERGY (e.v.)
S₂C₂H₂²⁻ (6π ELECTRONS)
ENERGY (e.v.)
2a₂
-13.6
2a₂
+0.52
2b₁
-16.4
2b₁
-10.2
1a₂
-25.1
1a₂
-11.9
1b₁
-26.3
1b₁
-12.8
S
C
+
-
CALCULATED BOND LENGTHS AND π BOND ORDERS (IN PARENTHESES)
1.61Å
1.47Å(0.26)
(0.86)
1.76Å
1.34Å(0.97)
(0.17)

FIG. 24: REPRESENTATIONS OF THE MOLECULAR ORBITALS AND ENERGY LEVELS FOR $S_2C_2H_2$ AND $S_2C_2H_2^{2-}$

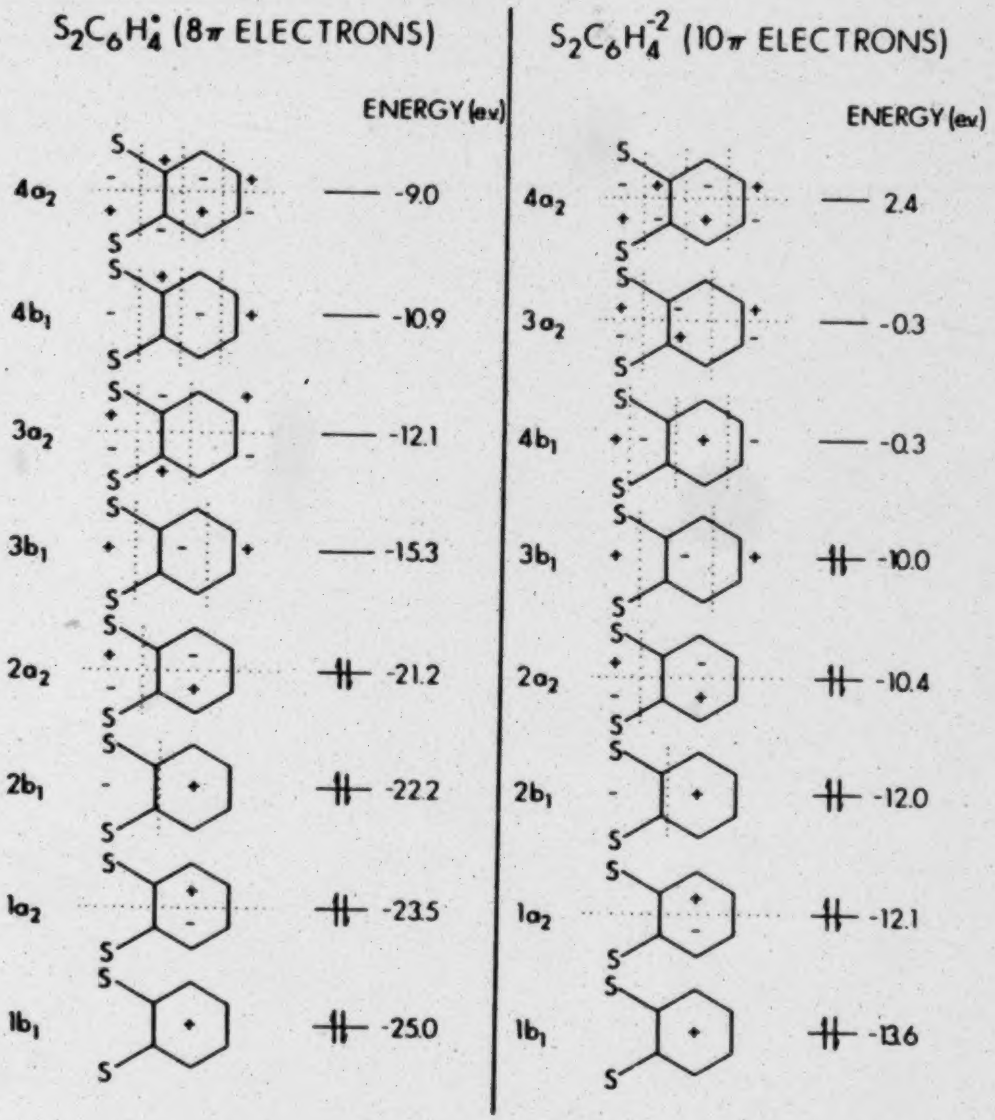
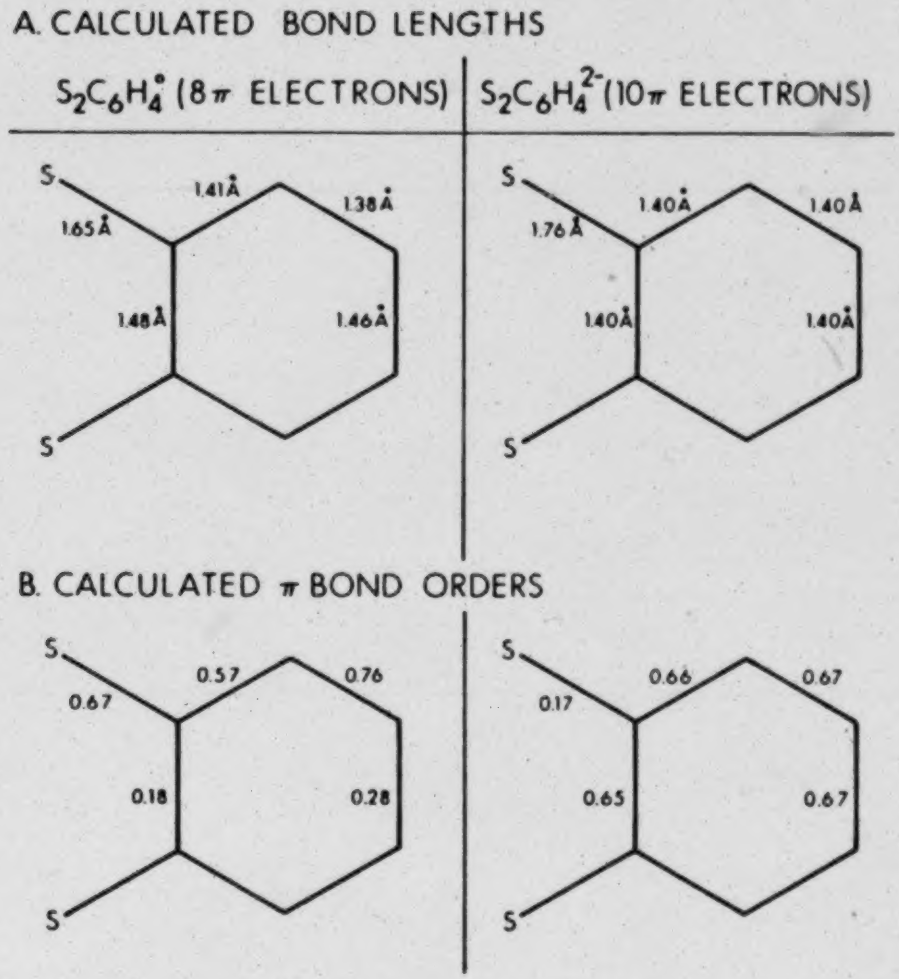

S2C6H4* (8π ELECTRONS)
S2C6H4-2 (10π ELECTRONS)
ENERGY (ev)
ENERGY (ev)
4a2 -9.0
4b1 -10.9
3a2 -12.1
3b1 -15.3
2a2 -21.2
2b1 -22.2
1a2 -23.5
1b1 -25.0
4a2 2.4
3a2 -0.3
4b1 -0.3
3b1 -10.0
2a2 -10.4
2b1 -12.0
1a2 -12.1
1b1 -13.6
S
+
-

FIG. 25: REPRESENTATIONS OF THE MOLECULAR ORBITALS AND ENERGY LEVELS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$



A. CALCULATED BOND LENGTHS

B. CALCULATED π BOND ORDERS

$S_2C_6H_4^{\bullet}$ (8π ELECTRONS)
$S_2C_6H_4^{2-}$ (10π ELECTRONS)
S
1.65Å
1.41Å
1.38Å
1.48Å
1.46Å
S
S
1.76Å
1.40Å
1.40Å
1.40Å
1.40Å
S
S
0.67
0.57
0.76
0.18
0.28
S
S
0.17
0.66
0.67
0.65
0.67
S

FIG. 26: PREDICTED BOND LENGTHS AND π BOND ORDERS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$

postulate, since in this isoelectronic series no change in the geometry of the coordination polyhedra can be attributed to the occupation of the antibonding orbitals, as has been postulated[141,170] for the destabilization of the prisms in $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$.

The 4e' level should be extremely sensitive to the metal d orbital energies due to the near-equivalence in energy of the d orbitals and the 4e' level. The $2a_1'$ level will also be affected but not as much, due to the greater energy separation of it from the metal d orbitals. As the d orbital energies increase, the 4e' level should be destabilized and should become more ligand ($3\pi_v$) in character. This increase in the ligand character of the 4e' level should be paralleled by a structural change, corresponding to an increase in the contribution of the reduced form structure. The molecular orbital description of the ligands is used in preference to the oversimplified valence bond descriptions, that is, the dithiolato and dithioketonic structures, shown in Fig. 11, since the discussion concerns energy levels and not just geometric changes.

The ligand undergoes extensive geometric changes upon the reduction:

$$S_2C_6H_4^{\circ}\ (8\ \pi\ \text{electrons}) + 2e \rightarrow S_2C_6H_4^{2-}\ (10\ \pi\ \text{electrons})$$

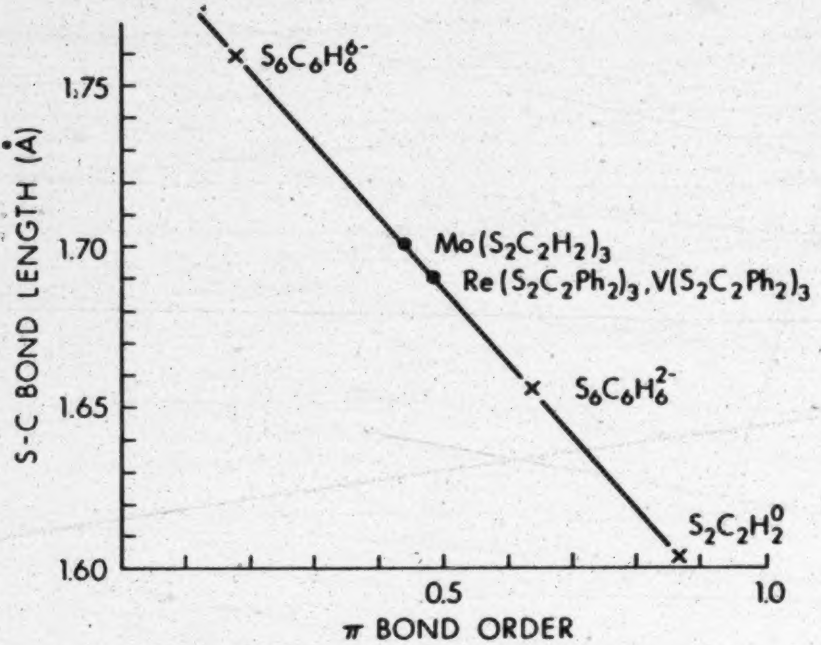
as is shown in Fig. 26. In principle, both sulfur-carbon and carbon-carbon distances could be used in assessing the relative importance of the reduced and oxidized structures in a particular case. In practice, the high uncertainty in the carbon-carbon bond lengths (due to naturally higher standard deviations and large effects due to thermal motion) makes them unsuitable for a semi-quantitative discussion and the more reliable sulfur-carbon distances provide the only useful guide. Sulfur-carbon bond lengths for the *tris* (benzene-1,2-dithiolato) complexes, described in this thesis, and the theoretical geometries of the oxidized and reduced formulations can be ordered as follows: $S_2C_6H_4^{\circ}$, (1.648 Å) < $Mo(bdt)_3$, (1.727 Å) < $Nb(bdt)_3^-$, (1.744 Å) < $Zr(bdt)_3^{2-}$, (1.765 Å) ≈ $S_2C_6H_4^{2-}$, (1.763 Å). This series indicates that the ligand tends toward the reduced geometry as the energy of the d orbital increases.

In assessing the ligand and metal orbital character of the 4e' level, it should be noted that appropriate extremes do not correspond to $[S_6C_{18}H_{12}]^{\circ}$ and $[S_6C_{18}H_{12}]^{6-}$ (equivalent to three ligands in the oxidized and reduced forms), since the ligand $3\pi_v$ orbitals give rise to the $2a_2'$ level as well as the 4e' level (see Fig. 23). This $2a_2'$ level is non-bonding, entirely located on the ligand and is always occupied by two electrons. Hence the discussion of the 4e' levels must utilize limiting geometries defined by $[S_6C_{18}H_{12}]^{2-}$ and $[S_6C_{18}H_{12}]^{6-}$, that is, allowing for the $2a_2'$ occupancy.

Fig. 27 shows the plots of S-C bond length *vs.* S-C π bond order for the ethylene and benzene dithiol ligands, as calculated by Birss and Das Gupta.[160] The limiting extremes, $S_2C_2H_2$ and $S_2C_2H_2^{2-}$, also $S_2C_6H_4$ and $S_2C_6H_4^{2-}$, are shown on the respective plots. For the ligand system $S_6C_{18}H_{12}^{2-}$, the π bond order and bond length can be calculated assuming one contribution of $S_2C_6H_4^{2-}$ for two contributions of $S_2C_6H_4$ This yields a S-C π bond order of 0.50 and a corresponding S-C bond length of 1.69 Å. If the 4e' levels are completely ligand in character, the ligand $3\pi_v$ orbitals would contain 6 electrons and would be described as $S_6C_{18}H_{12}^{6-}$. The S-C π bond order and S-C bond length for this extreme are 0.17 and 1.76 Å respectively. These two limits, $S_6C_{18}H_{12}^{2-}$ and $S_6C_{18}H_{12}^{6-}$, then correspond to the extremes that the 4e' orbital is completely metal and completely ligand in character, respectively.

In $Mo(bdt)_3$ the average S-C bond length (1.727 Å) corresponds to a π bond order of 0.32 and thus lies

(A) Ethylene Dithiol Ligands



(B) Benzene Dithiol Ligands

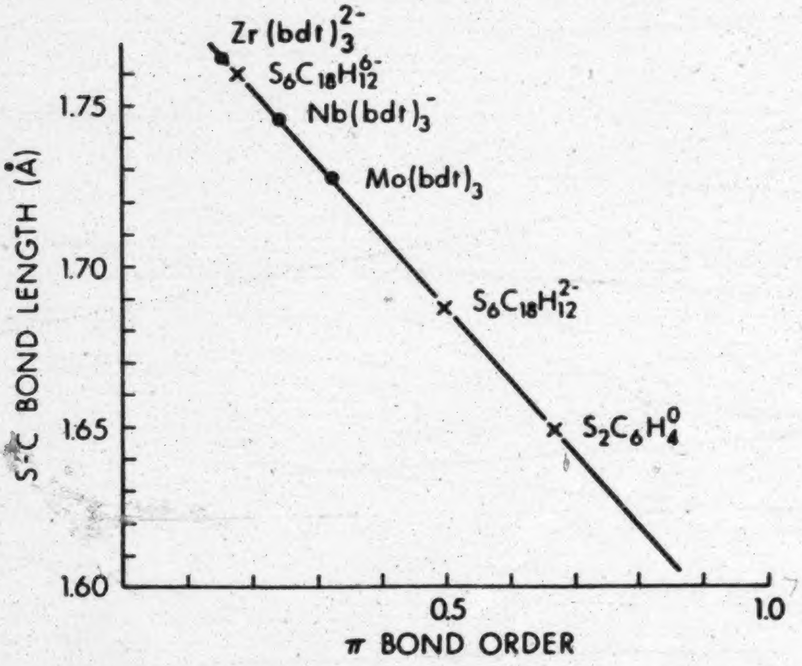


FIG. 27: S-C BOND LENGTH *vs.* π BOND ORDER FOR ETHYLENE AND BENZENE DITHIOL LIGANDS

approximately midway between the $S_6C_{18}H_{12}^{6-}$ and $S_6C_{18}H_{12}^{2-}$ extremes. The 4e' level therefore has approximately equal contributions from the metal and ligand orbitals. In $Nb(bdt)_3^-$ the S-C bond length of 1.744 Å and π bond order of 0.24 corresponds to three quarters of the electron density of 4e' being on the ligand and only one quarter of the electron density being on the metal. The S-C bond length of 1.765 Å in $Zr(bdt)_3^{2-}$ indicates that the ligand has reached the limiting reduced formulation. It is to be noted, however, that there is a tendency in the zirconium coordination toward the trigonal prism, indicating possibly that the 4e' level still has a small amount of metal contribution. It is also possible that the tendency toward the prism is favoured by the overlap of the ligand π_h and metal d_{z^2} orbitals, which may still be operative.

In Chapter V it was mentioned that any comparison in bond lengths between ethylene and benzene dithiol ligands should be made with extreme care. This can now be demonstrated with the aid of the calculations by Birss and Das Gupta,[160] shown in Fig. 27. In the ethylene dithiol ligands, employing similar arguments as used for the benzene dithiol ligands, the S-C bond lengths and π bond orders can be calculated for the $S_6C_6H_6^{2-}$ and $S_6C_6H_6^{6-}$ extremes. These bond lengths and π bond orders are 1.66 Å and 0.64 for $S_6C_6H_6^{2-}$ and 1.76 Å and 0.17 for $S_6C_6H_6^{6-}$. Thus although $Mo(S_2C_2H_2)_3$ has S-C distances (av. 1.70 Å) which are shorter than in $Mo(bdt)_3$, a comparison on Fig. 27 shows that in the two complexes the 4e' level has a similar make-up. It is therefore apparent that for different ligands, even in similar bonding situations, differences in bond lengths are to be expected.

The series of complexes, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$ therefore shows the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} with the ligand π_v orbitals in stabilizing the trigonal prism. In addition, the prism stability in this series is maximized in $Mo(bdt)_3$, where the 4e' orbital contains approximately equal contributions from metal and ligand and thus the electrons are completely delocalized over the metal-ligand framework. In the 1,1-dithiolato complexes[177-184] the ligands do not have orbitals of the proper symmetry and energy to overlap with the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal.[157] Therefore this delocalization is not possible and all 1,1-dithiolato complexes have distorted octahedral coordinations.

Interligand sulfur-sulfur bonding has also been presented as a reason for prism stability,[137,138,170] and the trends observed in the benzene dithiol series can also be explained by assuming that a breakdown in S-S bonding occurs, progressing from the molybdenum complex through to the zirconium complex. As the d energies increase, so also do the metal radii. Therefore, as the metal radii increase from Mo to Nb to Zr, the interligand S-S distances increase and the slight distortion observed in $Nb(bdt)_3^-$ can be explained as a partial breakdown in this S-S bonding. At $Zr(bdt)_3$ presumably the sulfur atoms have been forced far enough apart to result in a distorted octahedral coordination, due to an almost complete breakdown in S-S bonding. A significant argument, however, against sulfur-sulfur bonding as a major stabilizing force in the prism can be seen in a comparison of $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ with $Nb(bdt)_3^-$. In the niobium complex the interligand sulfur-sulfur distances are greater than those in the molybdenum or the tungsten dianions (see Table 48), yet the niobium complex is trigonal prismatic, whereas the dianions are distorted octahedrons.

The major argument for sulfur-sulfur bonding has been the short sulfur-sulfur contacts observed in the prisms, as compared with the predicted van der Waals contacts[151] (3.70 Å). However these contacts probably arise as a consequence of other factors which stabilize the prism, and are probably not themselves the reason for this geometry. It is believed that the forces between the sulfur atoms are repulsive in nature rather than attractive, as proposed.[137,138,170] This can offer a possible explanation for the geometry observed[132] in $V(S_2C_2Ph_2)_3$, which is distorted slightly from the prism by a trigonal twist of 8.5°. If, as suspected, the prism dimensions in the rhenium and molybdenum complexes[129,130] have reached their minimum, due to increasing S-S repulsions, then in the vanadium complex the smaller size of the metal could result in poor overlap of the metal and ligand orbitals (possibly ligand π_h with metal d_{z^2}). It is then possible that in order to attain the maximum stability, the prism distorts slightly by the observed trigonal twist. In this respect a complete structural determination of $Cr(S_2C_2Ph_2)_3$ is desirable, since X-ray power photographs indicated[128,129] it is isomorphous with $V(S_2C_2Ph_2)_3$. However, since the chromium radius is smaller than that of vanadium,[133] if the above arguments apply, the coordination of the chromium complex should be more distorted from the prism than the vanadium complex.

Any proposed sulfur-sulfur bonding can occur by two mechanisms: overlap of the sulfur p orbitals perpendicular to the ligand plane (π_v orbitals), or overlap of the non-bonding sulfur lone pair (π_h orbitals). It is not believed, however, that either mechanism has a significant effect in stabilizing the prism, since both types of overlap are possible in the 1,1-dithiolato systems, yet these systems invariably have geometries which are close to the "corrected" octahedral limit.

In conclusion, the importance of the 4e' molecular orbital in stabilizing the trigonal prism is evidenced in the series: $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$. The increasing energies of the metal d orbitals, progressing from the molybdenum to the zirconium complex, destabilizes the 4e' level, which in turn results in destabilization of the prism. Interligand sulfur-sulfur bonding is not believed to be a significant factor in stabilizing the prism.

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$$U_{ij} = \frac{\beta_{ij}}{2\pi^2 x_i x_j} \quad \text{where } x_1 = a^*,\ x_2 = b^* \text{ and } x_3 = c^*.$$

81. The equivalent isotropic B's are calculated from the expression $B = \frac{4}{3} \sum_{i,j=1}^{3} \beta_{ij} a_i \cdot a_j$ where the a_i and a_j are the translation vectors of the direct lattice.

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APPENDIX 1: MOLECULAR DISORDER IN TETRACARBONYL RHENIUM *BIS* (μ-DIPHENYLSILICON) RHENIUM TETRACARBONYL, $[Re_2(CO)_8[Si(C_6H_5)_2]_2]$.

The crystal and molecular structure of $Re_2(CO)_8[Si(C_6H_5)_2]_2$ was solved by X-ray diffraction techniques by Bennett and Haas.[64] The compound crystallizes in the monoclinic space group C2/m with two discrete molecules per unit cell, thus imposing site symmetry 2/m on the molecule. The unit cell dimensions are: $a = 13.976(3)$ Å, $b = 10.549(1)$ Å, $c = 12.025(3)$ Å, $\beta = 117.57(6)°$, giving an observed density 1.98(2) g cm^{-3}, which agrees well with the calculated value of 2.03 g cm^{-3}. A three dimensional representation of the molecule is shown in Fig. 28. The molecule bears a strong resemblance to the related hydrides $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, having an almost identical Re_2Si_2 framework. As in the hydrides, two mutually *trans* carbonyl groups on each rhenium atom are perpendicular to the Re_2Si_2 plane. The other carbonyl groups are approximately *trans* to the Re-Si bonds.

The crystals contain discrete and disordered molecules, the disorder involving the phenyl groups attached to each silicon atom. One phenyl ring is located approximately in the crystallographic mirror and the other lies approximately perpendicular

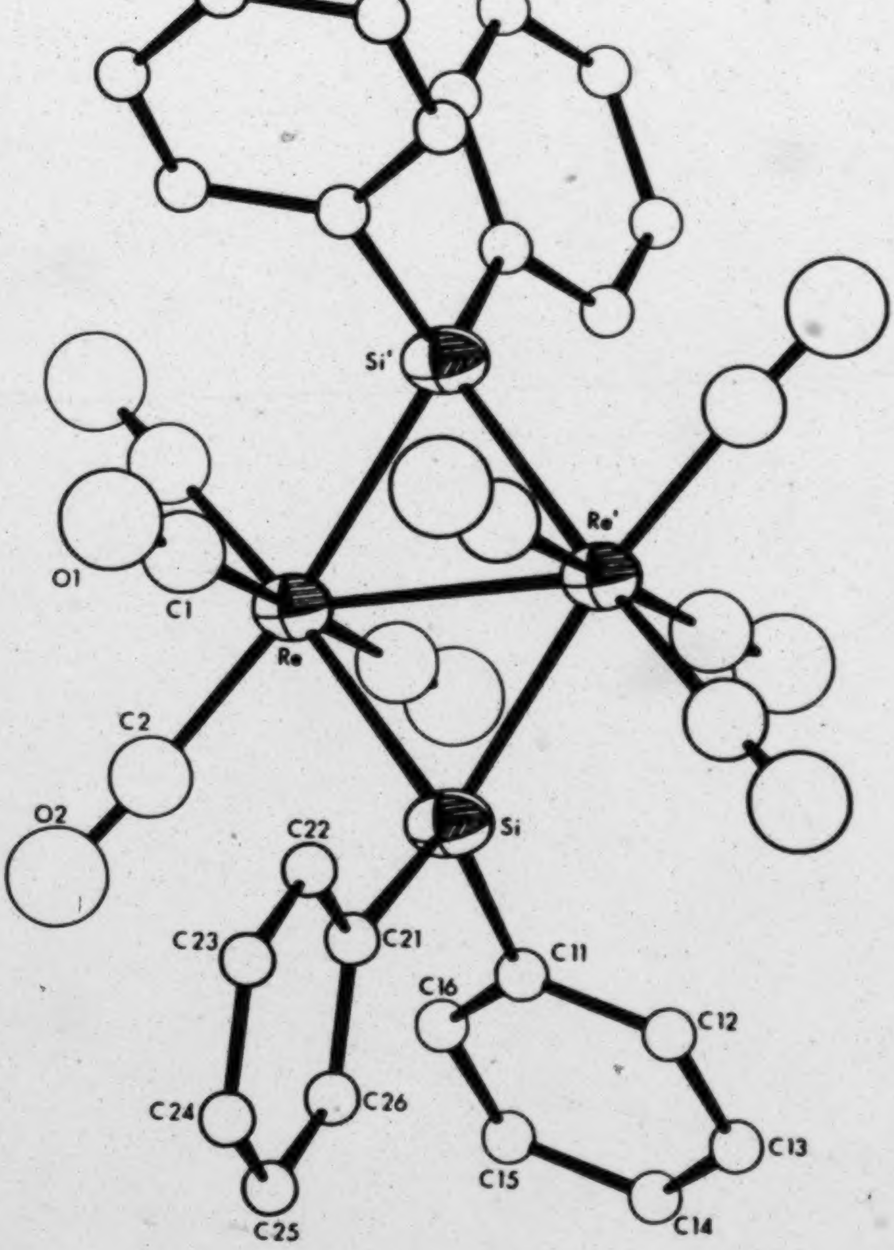

Si'
Re'
O1
C1
Re
C2
O2
C22
Si
C23
C21
C11
C16
C12
C24
C26
C13
C15
C14
C25

FIG. 28: A PERSPECTIVE VIEW OF $Re_2(CO)_8[Si(C_6H_5)_2]_2$

to it. Final refinement of this disordered model yielded $R_1 = 0.036$ and $R_2 = 0.057$ for 1153 independent reflections refining 52 parameters in the least squares refinement.

The final anisotropic thermal parameters (U_{ij}'s) for Re and Si are shown in Table 50, and the final positional parameters and the isotropic B's are shown in Table 51. Bond lengths and angles along with their standard deviations are shown in Table 52. In the representation of the molecule (Fig. 28) only one pair of disordered phenyl groups are shown for clarity. In addition the ring carbon atoms are given artificially low thermal parameters, also for clarity of the drawing.

The anomalously large values of U_{22} for both Re and Si were initially interpreted as due to residual absorption effects or other possible systematic errors in the data. However the structural determination[185] of the isomorphous $Mn_2(CO)_8[Si(C_6H_5)_2]_2$ shed new light on this problem. The manganese compound crystallizes in the space group A2/m with cell dimensions, $a = 11.788(2)$ Å, $b = 10.480(2)$ Å, $c = 13.744(2)$ Å and $\beta = 117.367(6)°$. (This is identical to C2/m with the *a* and *c* axes interchanged). Here again the phenyl rings are disordered in the same

TABLE 50: ANISOTROPIC THERMAL PARAMETERS FOR ORDERED MODEL

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0291(3)	0.0534(3)	0.0357(3)	0	0.0167(2)	0
Si	0.0314(13)	0.0660(17)	0.0364(13)	0	0.0157(11)	0

TABLE 51: POSITIONAL PARAMETERS AND ISOTROPIC B'S FOR ORDERED MODEL

Atom	x	y	z	B
Re	0	0.14224(3)	0	3.06*
Si	0.1388(2)	0	0.1678(2)	3.53*
C1	0.0724(8)	0.1448(6)	-0.1054(9)	4.04(15)
C2	0.1041(5)	0.2649(7)	0.1069(6)	3.99(12)
O1	0.1162(7)	0.1518(5)	-0.1686(8)	6.09(16)
O2	0.1682(7)	0.3414(6)	0.1658(7)	6.03(15)
C11	0.1424(8)	0.0146(13)	0.3289(6)	3.1(2)
C12	0.1265(10)	0.1262(10)	0.3807(10)	3.9(3)
C13	0.1301(10)	0.1237(10)	0.4987(10)	4.9(4)
C14	0.1496(8)	0.0097(13)	0.5649(6)	5.2(3)
C15	0.1655(10)	-0.1018(10)	0.5130(10)	5.1(3)
C16	0.1620(10)	-0.0994(10)	0.3950(10)	4.5(3)
C21	0.2854(15)	0.0165(13)	0.2008(34)	3.5(2)
C22	0.3172(22)	-0.0106(15)	0.1090(19)	3.9(2)
C23	0.4261(29)	-0.0043(14)	0.1382(21)	4.7(2)
C24	0.5033(15)	0.0292(13)	0.2591(34)	4.5(3)

Table 51 (con't)

Atom	x	y	z	B
C25	0.4715(22)	0.0563(15)	0.3509(19)	6.9(4)
C26	0.3626(29)	0.0500(14)	0.3218(21)	4.6(3)

*Equivalent isotropic temperature factor corresponding to the anisotropic thermal parameters shown in Table 50.

TABLE 52: SELECTED BOND LENGTHS AND ANGLES

(A) BOND LENGTHS (Å)

Re-Re	3.001(1)	Re-Si	2.542(3)
Re-C1	1.95(1)	Re-C2	1.93(1)
Si-C11	1.92(1)	Si-C21	1.91(1)
C1-O1	1.18(1)	C2-O2	1.17(1)

(B) ANGLES (DEGREES)

Re-Si-Re'[a]	72.3(1)	Si-Re-Si'	107.7(1)
C1-Re-C1'	178.4(4)	C2-Re-C2'	95.6(4)
C1-Re-C2	88.0(3)	C1-Re-Si	95.1(2)
C2-Re-Si	78.7(2)	C11-Si-C21	105.0(4)
C11-Si-Re	114.1(3)	C11-Si-Re	117.6(4)
Re-C1-O1	177.2(6)	Re-C2-O2	176.0(7)

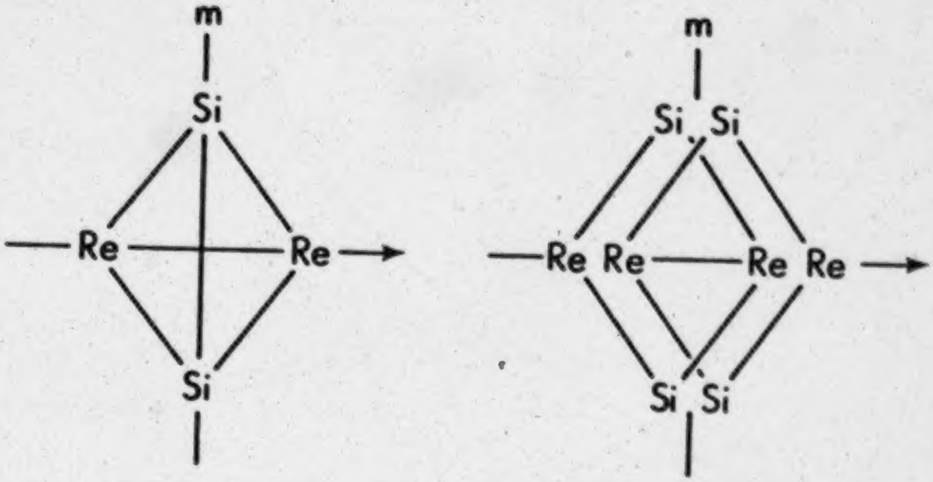
[a] Primed atoms are related by either the mirror plane or the two-fold axis, whichever is applicable.

way as the rhenium analogue. In addition the anisotropic thermal parameters for the metals and the silicon atoms are similar in the two compounds. It therefore seems unlikely that the anomalous thermal parameters in both compounds are due to systematic errors in the data.

It was believed possible that the disorder, observed in the phenyl groups, where the data permit resolution of the disorder, could reflect a disorder of the whole molecule. A proper assessment of this possible disorder becomes important then, in order to obtain unambiguous bond lengths and angles.

The high anisotropy in the heavy atom vibrational ellipsoids observed in both the rhenium and manganese compounds provided the clue to the mode of disorder. Since the major axes of the thermal ellipsoids in both compounds were much larger than the other axes, it was believed that the disorder involved slight displacements of the molecule along the crystallographic *b* axis, as shown in Fig. 29. The vibrational ellipsoids are certainly large enough to contain two distinct rhenium and silicon populations, separated from their disorder averaged positions by approximately 0.15 Å.

Thus the completely disordered model was refined



ORDERED

DISORDERED

Fig. 29: Mode of Disorder in $Re_2(CO)_8[Si(C_6H_5)_2]_2$.

to test whether it gave any better fit to the experimental data than the model involving an ordered Re_2Si_2 cluster. In the least squares refinement the parameters for the rhenium and silicon atoms were refined without restriction, other than that imposed by symmetry. However all the parameters for the carbon and oxygen atoms of the carbonyl groups were not refined due to correlations between the x and z coordinates of the two disordered molecules. Thus for one of the disordered forms all coordinates were refined while for the other molecule only the y coordinate was refined. After a cycle of refinement the x and z coordinates of the second molecule were set equal to those of its disorder-related mate and a further cycle was repeated with the same restrictions on the parameters. This was repeated until further iteration produced no significant shifts.

The final model had all atoms located at approximately 0.3 Å from their disorder-related partners. Thus the data were of good enough quality to differentiate the two disordered molecules although only 0.3 Å apart. The validity of the completely disordered model was verified by a Hamilton's R Test[79] at the 0.005 significance level, showing that the disordered model was significantly better than the ordered model. In the final least squares cycle $R_1 = 0.035$ and $R_2 = 0.056$ for 68 refined parameters. The anisotropic thermal parameters are shown in Table 53. The final positional parameters for all atoms in the completely disordered model are shown in Table 54 along with the isotropic B's of all atoms.

Electron density difference maps were also calculated for each model and were again found to be better for the completely disordered model with less residual electron density in its map. The highest peaks on each map were 1.39e $Å^{-3}$ and 1.11e $Å^{-3}$ for the ordered and disordered models respectively, this

TABLE 53: ANISOTROPIC THERMAL PARAMETERS FOR DISORDERED MODEL

Atom[a]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0274(6)	0.0215(17)	0.0353(6)	0	0.0157(4)	0
Re'	0.0304(6)	0.0211(18)	0.0361(6)	0	0.0175(4)	0
Si	0.0318(12)	0.021(7)	0.0370(12)	0.0000(12)	0.0158(11)	0.0000(13)

[a] Primed atoms are the disorder-related atoms.

TABLE 54: POSITIONAL PARAMETERS AND ISOTROPIC B'S FOR DISORDERED MODEL

Atom	x[a]	y	z	B
Re	0.0	0.1578(4)	0.0	2.18*
Re'	0.0	0.1266(3)	0.0	2.24*
Si	0.1387(2)	0.0178(11)	0.1678(3)	2.37*
C1	0.0743(11)	0.1594(19)	-0.1030(13)	3.3(4)
C1'	0.0743	0.1303(20)	-0.1030	3.5(5)
C2	0.1037(10)	0.2773(20)	0.1056(11)	2.9(5)
C2'	0.1037	0.2486(20)	0.1056	3.8(5)
O1	0.1169(10)	0.1697(16)	-0.1672(11)	5.0(4)
O1'	0.1169	0.1349 (16)	-0.1672	5.1(4)
O2	0.1674(13)	0.3450(17)	0.1639(13)	4.0(4)
O2'	0.1674	0.3308(25)	0.1639	8.7(6)
C11	0.1423(8)	0.0146(13)	0.3295(6)	3.1(2)
C12	0.1268(10)	0.1254(10)	0.3817(10)	4.1(3)
C13	0.1301(10)	0.1224(10)	0.4990(10)	4.9(4)
C14	0.1488(8)	0.0086(13)	0.5641(6)	5.2(2)
C15	0.1643(10)	-0.1022(10)	0.5119(10)	5.3(3)
C16	0.1610(10)	-0.0992(10)	0.3946(10)	4.7(3)
C21	0.2861(26)	0.0167(12)	0.2009(33)	3.5(2)
C22	0.3175(22)	-0.0094(15)	0.1092(19)	3.9(2)
C23	0.4259(29)	-0.0036(14)	0.1382(21)	4.6(2)
C24	0.5029(16)	0.0283(12)	0.2589(33)	4.6(3)

Table 54 (con't)

Atom	x	y	z	B
C25	0.4715(22)	0.0544(15)	0.3505(19)	6.5(4)
C26	0.3631(29)	0.0486(14)	0.3215(21)	4.4(3)

*Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 53.

[a] Where standard deviations are not given, the parameters were not refined.

density being located in the vicinity of the rhenium atoms in each map.

Thus although it seems that the data are best fitted using the disordered model, the initial ordered model (involving only disordered phenyl groups) is believed to provide a good description of the average geometry, and therefore bond lengths and angles obtained from this model are suitable. This is due to the mode of disorder which involves only a small translation of the whole molecule collinear with the Re-Re bond. The thermal parameters in this model cannot, however, be given any chemical significance since they (especially the U_{22}'s) reflect the disorder present. That the ordered model provides a good description of the average geometry of the molecule is also seen from the bond lengths and angles, which are all reasonable and in good agreement with the related molecules, $Re_2(CO)_8H_2Si(C_6H_5)_2$,[65] $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$.

APPENDIX 2: PROGRAMMES USED IN CRYSTAL STRUCTURE SOLUTION, REFINEMENT AND ANALYSIS

AUTHOR	PROGRAMME	DESCRIPTION
D. P. Shoemaker	MIXG2	Calculates Picker diffractometer settings from unit cell dimensions and cell type.
M. J. Bennett	PMMO	Transforms raw data to intensities, applying L_P corrections.
M. Elder and K. A. Simpson	D-REFINE	Refines cell parameters for all space groups.
A. Zalkin	FORDAP	Fourier summation for Patterson or Fourier maps.
W. C. Hamilton	GONO9 [a]	Absorption corrections for Picker data.
P. Coppens	DATAP [b]	Absorption and Extinction corrections.
C. T. Prewitt	SFLS5	Structure factor calculation and least squares refinement of parameters. Modified by B. M. Foxman and M. J. Bennett for rigid body routine, and by W. L. Hutcheon and M. J. Bennett for the hindered rotor.
J. S. Woods	MGEOM [a]	Calculates bond lengths, angles and best planes.
M. E. Pippy and F. R. Ahmed	NRC-22 [b]	Calculates least squares planes.
W. Busing and H. A. Levy	ORFFE	Calculates bond lengths, angles, and associated standard deviations; modified by B. Penfold for I.B.M. 360 and W. L. Brooks and M. Elder for hindered rotors and rigid bodies.

AUTHOR	PROGRAMME	DESCRIPTION
C. Johnson	ORTEP	Writes Plot Command for Calcomp plotter, for plotting three dimensional molecular representations. Calculates bond lengths and principal axes of anisotropic thermal motion.
M. J. Bennett and B. M. Foxman	MMMR	Calculates starting parameters for rigid bodies and hindered rotors.
M. Cowie	PUBE	Sorts data according to any desired sequence of h, k, or ℓ.
R. C. Elder	PUBTAB	Prints Structure Factor Amplitude Tables; modified by M. Cowie to work in conjunction with PUBE.
G. J. B. Williams	FRAME [c]	Converts continuous paper tape output from automatic diffractometer, in ASCII code to "framed" output on cards in EBCDIC coding, suitable for PMMO input.

[a] This programme was used for the two rhenium hydrides.

[b] This programme was used for the three tris dithiolene complexes.

[c] This programme was used only for $[Ph_4As][Nb(bdt)_3]$. In the other two structures collected by automatic diffractometer, magnetic tape output was used. This was translated from ASCII by a subroutine added to PMMO by myself.